Rare Metal Materials and Engineering
Volume 50, Issue 6, June 2021
Available online at www.rmme.ac.cn

Science Press

Cite this article as: Qi Chunbao, Wang Tao, Tao Sihao, et al. Progress on Surface Corrosion of Plutonium and Its Compounds[J]. Rare Metal Materials and Engineering, 2021, 50(06): 2008-2016.

REVIEW

Progress on Surface Corrosion of Plutonium and Its Compounds

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Abstract: In order to acquire the mechanism of surface oxidation corrosion of plutonium (Pu) and its compounds and explore the environmental system that can effectively alleviate the oxidation corrosion of plutonium materials, some research results on surface chemistry of plutonium and its compounds were reviewed, which deepen the understanding of the corrosion behavior of plutonium and its compounds in the air. The adsorption behavior of active gases such as H_2, O_2, CO, CO_2 and H_2O (gaseous) and rare gases such as Xe on different surfaces of plutonium and its compounds was compared and analyzed, and some useful conclusions were obtained. It is concluded that the interaction of plutonium with various active gases and rare gases is accompanied by charge transfer, and the mechanism of reaction is mainly that the new chemical bonds are formed because of the interaction between the different hybrid orbitals of gas atoms (or molecules) and plutonium atoms such as Pu7s, Pu6p, Pu6d and Pu5f, which leads to related reactions and phenomena. The research work prospect on the surface corrosion of plutonium and its compounds is also taken from three aspects including improving research methods, carrying out research on other surface adsorption behavior of plutonium atoms and exploring new systems for protecting plutonium materials from oxidative corrosion.

Key words: plutonium surface; active gas; density functional theory; electron density; adsorption behavior; reaction mechanism

Plutonium is one of the most complex elements in the periodic table of elements. It is located between light actinide elements (Th to Pu, 5f electrons of which have itinerant properties) and heavy actinide elements (Am and subsequent elements, 5f electrons of which have locality). As an important functional material, plutonium is used widely in the fields of military, energy and aerospace. Due to its complex 5f electronic state[1] and lower locality than that of uranium [2], plutonium shows many different properties from metallic uranium and many special physical properties. Between room temperature and its melting point, pure metallic plutonium has six phase structures[3]. At present, we are most concerned with δ-phase Pu which is formed in a stable state with a small amount of Al and Ga because of the good mechanical properties and metal properties[4]. The chemical properties of plutonium are very active and it is easy to react with the gases such as H_2, O_2, CO and CO_2 during purification, storage and use. It brings great difficulties to the protection of plutonium materials and may also cause serious environmental pollution.

Plutonium scientists[5-7] has focused on the surface chemistry of plutonium. Adsorption of active gas on plutonium surface is a necessary process for hydrogenation and oxidation corrosion. In fact, the reactions between plutonium and elements such as C, H, O and N in the environment are completed through surface chemical adsorption and physical adsorption[8,9]. Because surface corrosion of plutonium is inevitable, it faces many difficulties in storage and use of plutonium metal and plutonium containing materials. Generally speaking, there are several oxides of PuO, PuO_2 and Pu_2O_3 and other oxides and mixed crystals on the surface of metallic plutonium, where PuO and PuO_2 are the basic products of plutonium surface oxidation[5,6,10,11]. During the corrosion process of plutonium alloy, the physical and chemical state of its surface oxide plays a very important role[4,12-14]. The physical and chemical behavior of different kinds of surface oxide varies greatly, and the further corrosion effect on plutonium is also different. Thus, it is an important research content in the fields of plutonium material corrosion

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Received date: June 18, 2020

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protection, nuclear waste disposal, storage and aging to study the interaction properties of plutonium and its compounds with small molecules of gas and to reveal the microscopic chemical reaction mechanism. Because plutonium has special properties, hypertoxicity and radiation hazards, it is difficult to carry out experimental research. Therefore, to understand the surface corrosion of plutonium materials and to reveal the corrosion mechanism of plutonium, we must understand the surface properties of plutonium as well as the adsorption and dissociation of various gases on the surface of plutonium theoretically.

In this work, the surface corrosion of plutonium and its compounds all over the world was reviewed, summarized and looked forward to. The adsorption behavior of reactive gas and rare gas on the surface of plutonium and its compounds was also compared and analyzed, and the microscopic reaction mechanisms of their interaction were summarized, which are helpful to deepen the understanding of the corrosion process of plutonium materials and lay the foundation for exploring the environmental system that can passivate or alleviate the corrosion of plutonium materials.

1 Corrosion Behavior of Plutonium and Its Compounds in Air

In 1960, Coffinbery et al[15] found that the oxidation rate of plutonium in air was related to relative humidity by experiment. In 1998, Haschke et al[16] concluded that the corrosion of plutonium in air was catalyzed by hydrogenated plutonium on the metal surface by kinetic method, and showed that this process led to the failure of storage containers. The catalytic reaction starts at 25 °C, consuming O_2 and N_2 indiscriminately, and converting the metal into a dispersible product at a rate of 10^7~10^{10} which is faster than normal air oxidation. Haschke et al[17,18] studied the high-speed oxidation mechanism of plutonium materials in humid air. As water was adsorbed and dissolved on the surface of plutonium, hydrogen and plutonium oxide were generated. On the one hand, the generation of hydrogen led to the rupture of the PuO_2 protective layer; on the other hand, hydrogen penetrated the crack on the oxidation protective layer and reacted with Pu rapidly to generate hydride PuH, which was crystallizing and nucleating. The hydrogenation rate increased exponentially with the crystallization nucleation area. At the same time, an inward diffusion oxygen gradient formed by the adsorption of oxygen on the outer surface of the oxide led to the formation of water catalytic reaction. Finally, the corrosion rate of plutonium materials in humid environment increased by thousands of times. Research by Hecker et al[19] showed that plutonium corrodes abnormally rapidly in humid atmosphere. The oxidation corrosion rate can reach 200 times of that in dry air at room temperature and 100 000 times of that in dry air at 700 °C. According to the research by Haschke et al[20] on the interaction of plutonium dioxide with water vapor and oxyhydrogen mixture, the corrosion rate was controlled by the same process of oxygen diffusion through the oxide layer on the metal surface in all cases. With the adsorption and dissociation of water, the gradient of oxygen concentration on the oxide layer was changed, and the corrosion rate was also changed.

In 2002, the dynamics research results of Pu+HO, H+PuO and O+PuH by Meng[21] showed that the reactions Pu+HO→PuO+H and O+PuH→PuO+H were all remarkable exothermic reactions without threshold energy, and the products were almost PuO+H. On the contrary, H+PuO was mainly a non-reactive process, i.e. the main product was H+PuO, which was also consistent with the experimental conclusion that the reaction rate of metal plutonium with air was greatly increased in the presence of hydride catalysis. Chen et al[22] studied on the adsorption behavior of water on PuO_2 surface using kinetic Monte Carlo simulation method, and obtained the desorption activation energy of water as: 200 kJ/mol for 0~0.5 layer, 135 kJ/mol for 0.5~1 layer , 47.6 kJ/mol for 1~2 layer, 43.8 kJ/mol for 2~3 layer, and 41.1 kJ/mol for after 3 layers. The comparison between calculated and experimental values using fitting parameters is shown in Fig.1. Haschke[23] measured the corrosion data of plutonium in the temperature range from 35 ℃ to 400 ℃ by kinetic method, and the results showed that the humidity dependence of the corrosion rate of non-alloy plutonium in air or oxygen-containing atmosphere was restricted in the temperature range from 25 ℃ to 200 ℃, and the temperature at the maximum corrosion rate was close to 110 ℃.

2 Adsorption Behavior of Gases and H_2O on the Surface of Plutonium and Its Compounds

2.1 Adsorption behavior of H_2 on the surface of plutonium and its compounds

In 2010, Wei[24] studied the adsorption behavior of H_2 on δ-Pu(100) surface by density functional theory combined with flat periodic model. The results showed that the adsorption stability of H_2 molecules on δ-Pu(100) surface was hole site> bridge site>top site, and the vertical adsorption was more stable than the parallel adsorption at the same adsorption site. The adsorption of H_2 molecules on δ-Pu(100) surface was a

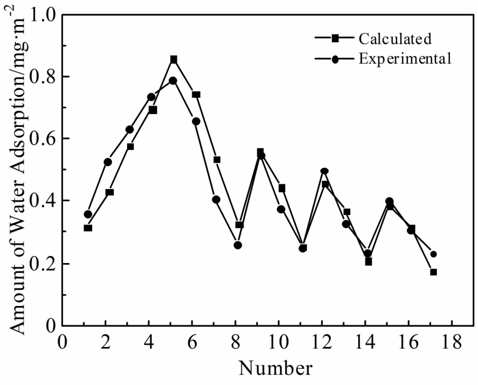

Fig.1 Comparison of calculated and experimental results[22]

weak physical adsorption. The adsorption of H_2 molecules tended to dissociate into the adsorption of two H atoms, and at this time, the adsorption was a strong chemical adsorption. The different configurations of H_2 adsorbed at the hole site on δ-Pu(100) surface are shown in Fig.2.

In 2018, Luo[25] calculated and analyzed the interaction between plutonium and hydrogen by the density functional theory and the relativistic effective core potential (RECP) with Gaussian09 program. The electron density correlation properties of all special structures in the reaction path were analyzed, and the detailed changes of electron density in the reaction process were obtained. Spin density equivalent surface and contour of special points along reaction pathway are shown in Fig.3.

2.2 Adsorption behavior of O_2 on the surface of plutonium and its compounds

In 2004, Huda[26] used the GGA-DET with Perdew and Wang (PW) function to study the oxygen adsorptions on δ-Pu (100) and δ-Pu(111) surfaces at both non-spin-polarized and spin-polarized levels. The central position of δ-Pu(100) surface was the most favorable site with chemisorption energies of 7.386 and 7.080 eV at two levels of theory. The distances between the oxygen adatom and the plutonium surface were found to be 0.092 and 0.102 nm. For non-spin-polarized calculation on δ-Pu(111) surface, the central position was also the optimal site with a chemisorption energy of 7.070 eV and the distance of the adatom being 0.131 nm. However, for spin-polarized calculations, it was found that the bridge and center sites were basically degenerate, and the difference in chemisorption energy was only 0.021 eV. Generally speaking, compared with the bare plutonium layer, the plutonium 5f orbitals were pushed further below the Fermi level due to the adsorption of oxygen. In general, the work function increased due to oxygen adsorption on the plutonium surface. The different chemisorption positions for δ-Pu(100) and (111) surface are shown in Fig.4.

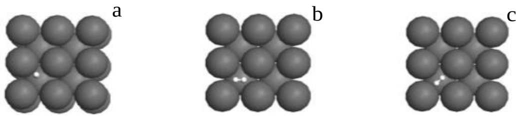

Fig.2 Top view of different configurations of H_2 adsorbed at the hole site on δ-Pu(100) surface[24]: (a) vertical adsorption, (b) parallel adsorption of P1, and (c) parallel adsorption of P2

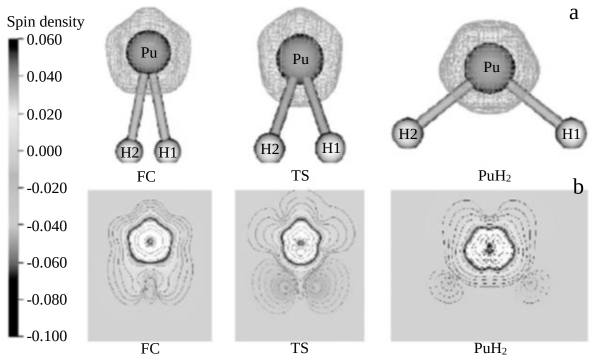

Fig.3 Spin density equivalent surface (a) and contour (b) of special points along reaction pathway[25]

In 2005, Huda[27] also used the GGA-DET to study the adsorption of oxygen molecules on δ-Pu(100) surface in detail. Compared to molecular adsorption, the dissociative adsorption with a layer by layer alternate spin arrangement of the plutonium layer was found to be energetically more favorable. Hor2 approach on a bridge site without spin polarization was found as the highest chemisorbed site with an energy of 8.787 eV among all the cases. Spin polarization affected the chemisorption processes significantly, so non-spin-polarized chemisorption energies were usually higher than spin-polarized energies. The 5f electrons were more localized in the case of spin-polarized compared to the non-spin-polarized counterparts. The ionic part of O-Pu bonding plays an important role, while Pu 5f-O 2p hybridization was found to be very weak.

In 2009, Wei[28] used the GGA-DET with RPBE functions to study the adsorption behavior of atomic oxygen on δ-Pu(111) surface at both spin-polarized level and non-spin-polarized level. The results showed that the adsorption of atomic oxygen on δ-Pu(111) surface belonged to strong chemical action. The number of Pu atoms coordinated with atomic oxygen was the main factor that determined chemisorption, and the more the number of coordination, the more stable the chemical bonding. Mulliken charge distribution analysis indicated that the interaction of Pu with O mainly took place in the first layer and that the other two layers were affected only slightly. In 2013, Guo[29] studied the adsorption behavior of O_2 molecules on δ-Pu(100) surface by GGA-DET at both the spin-polarized level and the non-spin-polarized level. The results showed that when O_2 was adsorbed on δ-Pu surface, the molecular bond length increased and eventually broke, dissociating into two atomic oxygen states for adsorption, and the dissociated oxygen atoms were preferentially adsorbed at the center and bridge sites.

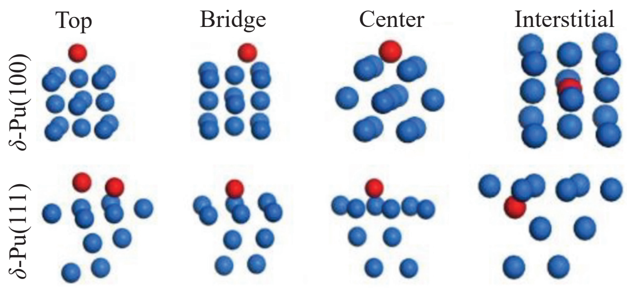

Fig.4 Different chemisorption positions for δ-Pu(100) surface and δ-Pu(111) surface[26]

2.3 Adsorption behavior of CO on the surface of plutonium and its compounds

In 1999, according to the calculation of the temperature dependence of standard Gibbs free energy change, ΔG^0, of the reaction of CO and H_2 with Pu, PuO, Pu_2O_3 and PuO_2, Li[30] proposed that the CO-H_2 system enabled a passive surface film to form on the compact and stable crystal surface of Pu_2O_3 to prevent the metallic plutonium from further corrosion by the inward diffusive CO and H_2 gas. It is presumably like the protecting aluminum surface with its oxidized layer. In 2001, Xue[31] pointed out that the reaction system of hydrogenated plutonium and CO had seven independent component, four chemical elements, so the plutonium hydride CO system involves of three independent reaction equations. The equilibrium compositions of CO(g), CO_2(g) and H_2(g) in simultaneous reaction and single reaction were calculated. It was shown that the simultaneous reactions had coupling effect and low temperature was in favor of the transformation of CO (g) and the production of Pu_2O_3(s).

In 2008, Luo[32] used DFT to study the adsorption of CO molecules on δ-Pu(100) surface. The calculation results showed that the C-down adsorption was more stable than the O-down adsorption, which was found to be a strong chemisorption. The stability of adsorption configuration of CO was hollow tilted>hollow vertical>bridge>on-top. The adsorption state of CO on δ-Pu(100) surface is shown in Fig. 5. From 2009 to 2011, Xiong's research results[33-35] showed that the most stable adsorption configuration of CO on Pu(100) and δ-Pu (111) surfaces was C-side center vertical position, which belonged to a strong chemisorption. It was concluded that the main factor that determined chemisorption was the coordination numbers of CO and Pu, and the more coordination numbers the Pu atoms, the more stable the chemical bonding. The Mulliken charge analysis showed that the surface interaction of CO and Pu mainly occurred in the first layer.

2.4 Adsorption behavior of CO_2 on the surface of plutonium and its compounds

In 2009, Meng[36] studied the adsorption and dissociation of CO_2 molecules on δ-Pu(100) surface using the revised Perdew-Burke-Ernzerh method of generalized gradient DFT combined with periodic slab model. The optimized results of adsorption energies and geometrical structures showed that the H-C4O4-type adsorption was optimum adsorption mode. The calculated activation barrier and adsorption energy of $CO_2 \rightarrow CO+O$ dissociative reaction were 0.66 and 2.65 eV, respectively, indicating that the dissociative adsorption of CO_2 on δ-Pu(100) surface was favorable under the certain heat activation condition. The initial state, transition state and final state of the dissociation process of $CO_2 \rightarrow CO+O$ on δ-Pu(100) surface are shown in Fig.6. Atta-Fynn[37] used ab initio calculation method and Dmol3 program within the framework of density functional theory to study the adsorption and dissociation behavior of CO_2 molecules on δ-Pu(111). The results showed that the fully dissociated configuration (C+O+O) showed the strongest binding to the surface (7.92 eV), followed by the partially dissociated configuration CO+O (5.08 eV), with the lowest binding energy of CO_2 molecules adsorption (2.35 eV). In 2014, Wang[38] used GGA-DFT and the suite of software DMOL3 and WIEN2k to study adsorption of CO_2 on α-Pu (020) surface nanolayer. The results showed that the completely dissociated configurations (C+O+O) exhibited the strongest binding with the surface (7.94 eV), followed by partially dissociated (CO+O) and CO_2 molecular configuration (5.18 and 1.90 eV, respectively). The difference charge density plots of CO_2 on α-Pu(020) surface for three most stable adsorption cases are shown in Fig.7.

2.5 Adsorption behavior of rare gases on the surface of plutonium and its compounds

In 2013, Chen[39] studied the adsorption of rare gas atoms including He, Ne, Ar, Kr and Xe on the surface of δ-Pu(100) using the first-principles. The calculation results show that the most stable adsorption sites for rare gas atoms except He atoms are bridge sites. After rare gas atoms are adsorbed on the surface of δ-Pu(100), they lose charge, while Pu atoms get charge, and Xe atoms in the rare gas atoms have the largest charge transfer number. The adsorption model of RG/Pu(100) system is shown in Fig.8.

2.6 Adsorption behavior of H_2O on the surface of plutonium and its compounds

In 2001, Wu[40] used DFT to study the electronic and geometric structures of prototype d- and f- electronic systems. The electronic and geometric structures of PuO_2 and its (110) surface, as well as the adsorption of water on this surface were also investigated by DFT in both local density approximation (LDA) and generalized gradient approximation (GGA)

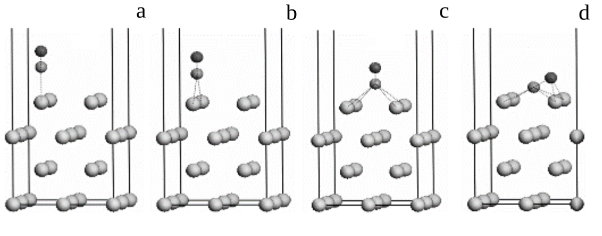

Fig.5 Adsorption state of CO on δ-Pu(100) surface[32]: (a) on-top, (b) bridge, (c) hollow vertical, and (d) hollow titled

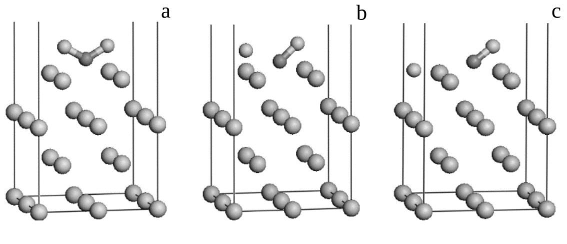

Fig.6 Initial state (a), transition state (b) and final state (c) of the dissociation process of $CO_2 \rightarrow CO+O$ on δ-Pu(100) surface[36]

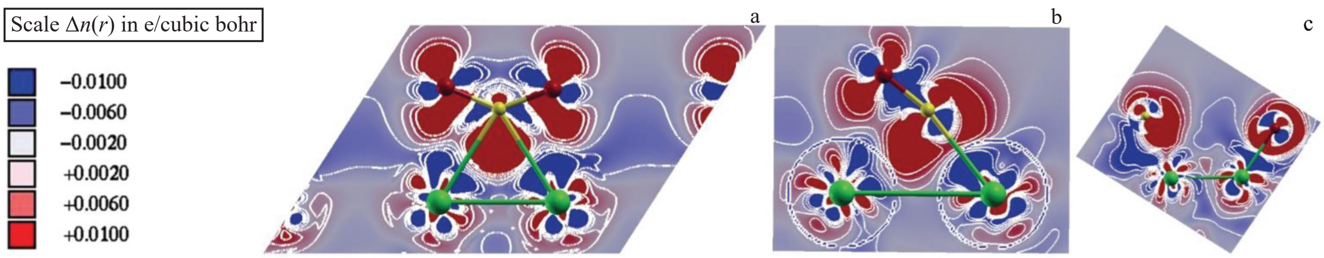

Fig.7 Different charge density plots of CO_2 on α-Pu(020) surface for three most stable adsorption cases: (a) molecular CO_2 adsorption, (b) partially dissociated (CO1+O2) adsorption, and (c) completely dissociated (C+O1+O2) adsorption[38] (red (positive) denotes regions of charge accumulation and blue (negative) denotes regions of charge depletion; Pu, O and C atoms are colored with green, red and gold, respectively)

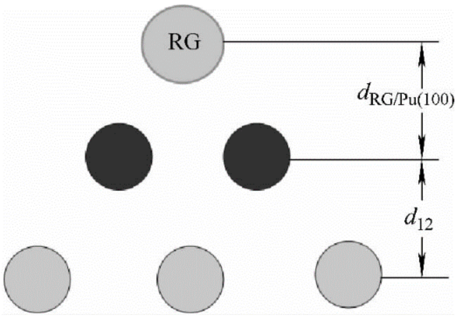

Fig.8 Adsorption model of RG/Pu(100) system[39]

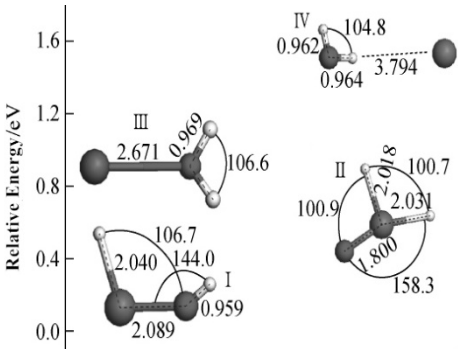

Fig.9 Equilibrium geometrical structures of plutonium-water compound[43]

formalisms using periodic models. In 2009, Atta-Fynn[41] carried out density functional calculations on the adsorption of water on Pu(111) surface, and it was believed that chemical adsorption would lead to the reduction of work function on the surface of plutonium. In 2010, the research results given by Wei[42] showed that the adsorption of water on δ-Pu(100) and δ-Pu(111) surfaces was both weak physical adsorption. And the adsorption was mainly determined by H atom and the first layer atom of Pu, where the H atom was preferentially adsorbed on the core site and bridge site. In 2012, Chen[43] used DFT with B3LYP methods to optimize the energy of several geometric structures composed of plutonium and water molecules system. Four structures of Pu-water system were proposed and studied, which are shown in Fig. 9. The thermodynamic functions of adsorption and dissociation reactions of metal Pu and H_2O at different temperatures were calculated. The results showed that the water vapor molecule cannot form adsorption on the surface of metal plutonium even at low temperatures. On the contrary, dissociation reactions of water molecule on the surface of metal plutonium occurred spontaneously.

3 Comparative Analysis of Adsorption of Various Gases on Plutonium Surface

In this study, the adsorption behavior of H_2, O_2, CO, CO_2 and H_2O on different surfaces of Pu is compared and analyzed, especially the adsorption position, geometric configuration, adsorption energy and work functions. It can be seen as the theoretical support for revealing the interaction mechanism between Pu and environmental gases (rare gases are not considered for the time being). Table 1 shows the most favorable adsorption position, geometric configuration, molecular bond length, dissociation energy and surface work functions of H_2, O_2, CO, CO_2 and H_2O on different Pu surfaces without spin polarization.

From Table 1, it can be seen that in different references[24,42,44], H_2 and H_2O have less electron transfer when adsorbed on δ-Pu(100) and δ-Pu(111) surfaces. It also showed that no new chemical bonds were formed and H-H and H-O bond lengths had little change compared with experimental values (0.074 and 0.0968 nm). Furthermore, the value of adsorption energy was also small, so the adsorptions of H_2 and H_2O on δ-Pu(100) and δ-Pu(111) surfaces were based on Van der Waals force physical adsorption. However, O_2, CO and CO_2 have more electron gained and lost on different surfaces of Pu with the O-O bond broken, the C-O bond length increased, and a higher adsorption energy. Therefore, O_2, CO and CO_2 have strong chemisorption on different surfaces of Pu. Among them, the adsorption energy of O_2 is the largest, and the absolute values of adsorption energy of CO and CO_2 are similar, but CO has a lower dissociation energy barrier and is easy to dissociate. From the view of adsorption energy, the

Table 1 Adsorption types and parameters of H_2, O_2, CO, CO_2 and H_2O on different surfaces of Pu

Substance	Surface	Adsorption position	Geometric configuration	R/nm	q/e	E_{deb}/eV	E_{ads}/eV	E_{diss}/eV	Φ/eV
H_2[24]	Pu(100)	H	Vertical hole	0.0756	0.114	-	0.183	1.169	4.403
H_2[44]	Pu(100)	H	Center vertical	0.0738	-0.05	0.78	0.150	1.03	-
O_2[29]	Pu(100)	O	Bridge 2	0.3250	-1.29	0.32	8.146	8.24	4.886
CO[32]	Pu(100)	C	Hollow tilted	0.1372	0.462	0.28	1.371	3.164	-
CO[35]	Pu(100)	C	Center vertical	0.1230	-	-	-1.780	-	5.007
CO[33]	Pu(111)	C	Center vertical	0.1208	0.082	-	-1.236	-	5.361
CO_2[36]	Pu(100)	C	Center vertical	0.1373	-0.79	0.66	1.48	2.65(CO_2→CO+O) 4.44(CO_2→C+O+O)	-
CO_2[37]	Pu(111)	C	Center vertical	0.1350	-	-	1.69	5.85(CO_2→CO+O) 4.34(CO_2→C+O+O)	3.39
CO_2[38]	Pu(020)	C	Long bridge	0.1280	-	-	1.46	5.08(CO_2→CO+O) 7.72(CO_2→C+O+O)	3.53
H_2O[42]	Pu(100)	H	Top center	0.9900	0.383	-	0.135	-	4.977
H_2O[42]	Pu(111)	H	Parallel bridge	0.9840	0.387	-	0.089	-	5.156

Note: plutonium surface refers to different plutonium surfaces, except Pu(020) surface is α-phase plutonium, and the rest is δ-phase plutonium; adsorption position refers to the most favorable adsorption position; geometric configuration is the most favorable geometric configuration; R is the bond length of the molecule; q is the net charge of the molecule; E_{deb} is dissociation energy barrier; E_{ads} is the adsorption energy of molecules; E_{diss} is the dissociation energy of molecules; Φ is surface work function

order of adsorption intensity of the five substances on different surfaces of Pu is O_2>CO>CO_2>H_2>H_2O at a low temperature. H_2 and CO_2 are easy to be thermally activated and thus dissociative adsorption occurs when the temperature is high. Therefore, the order of adsorption intensity of the five substances on different surfaces of Pu is O_2>CO_2>CO>H_2>H_2O from the perspective of dissociative energy. The above results show that Pu is the most easy to react with O_2 and the most difficult to react with H_2O in environmental atmosphere.

4 Surface Reaction Mechanism of Plutonium with Gases and Water

Luo's research [25] showed that the microscopic reaction mechanism of Pu and H_2 was Pu+H_2→FC→TS→PuH_2. Electronic domain function equivalent surface of all special points along reaction pathway is shown in Fig.10. This reaction is a microscopic chemical reaction process, in which the H-H bond length increases continuously to fracture.

Wei's research[28] showed that O atom was strongly chemisorbed on the surface of plutonium. The microscopic mechanism of the reaction was the hybridization of O 2p with Pu 7s, Pu6d and Pu5f orbitals. The partial electron density of states (PDOS) when O atom was adsorbed on the δ-Pu(111) surface is shown in Fig.11. The kinetic study of plutonium corrosion in O_2 atmosphere showed that Pu_2O_3 was generated in the initial surface reaction and then oxidized to PuO_2, which indicated that PuO_2 was the most stable in O_2 atmosphere, conforming to the general law of actinide oxidation and reduction[45].

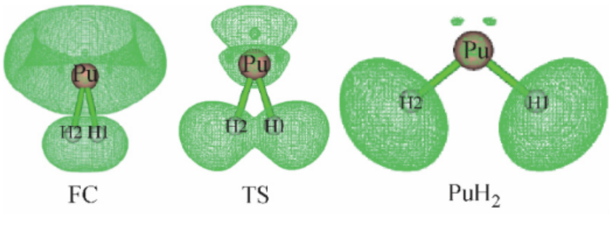

Fig.10 Electronic domain function equivalent surface of all special points along reaction pathway [25]

Luo's research[32] showed that the microscopic mechanism of the interaction between CO molecules and Pu atoms surface was that the C2s, C2p, O2s and O2p hybrid orbitals interacted with Pu 7s, Pu 6d and Pu 5f hybrid orbitals to form new chemical bonds. The partial electron density of atoms and dissociation adsorption of CO molecules on Pu(100) surface is shown in Fig.12. Researches [33-35] studied by Xiong Xiaoling showed that the microscopic mechanism of the interaction between CO and Pu(100) surface was that the 4σ, 5σ and 2π* orbitals of CO molecules interacted with Pu7s, Pu6p, Pu6d and Pu5f hybrid orbitals to form new chemical bonds.

The study of Meng[36] showed that the interaction mechanism between CO_2 and Pu(100) surface was mainly that the hybridization orbitals $2\pi_\mu$ of CO_2 molecules interacted with Pu 7s, Pu 6d and Pu 5f orbitals through strong electron transfer and weak overlapping hybridization to form new chemical bonds. The partial density of states of CO_2 molecules and surface Pu atoms after the most favorable molecular adsorption (h-C4O4) and dissociation adsorption of CO_2 on Pu (100) surface are shown in Fig.13.

Chen's research[39] showed that the interaction mechanism between different rare gas atoms and δ-Pu(100) surface was

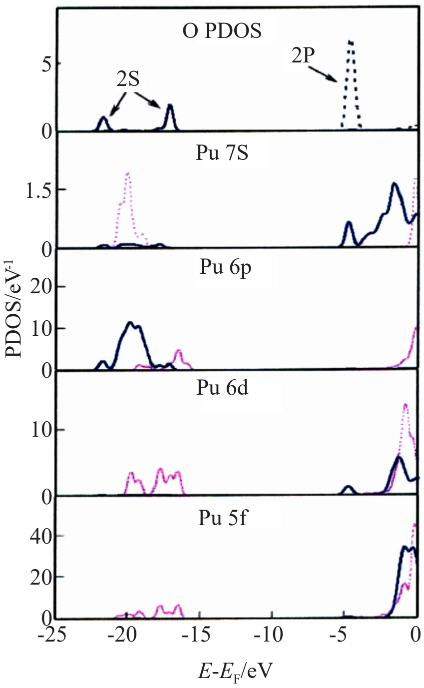

Fig.11 PDOS of oxygen atom adsorption on δ-Pu(111) surface[28]

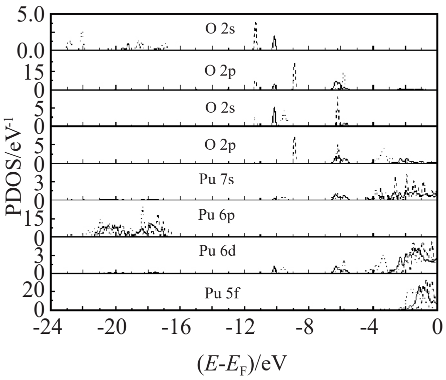

Fig.12 PDOS of dissociation adsorption of CO molecules on Pu (100) surface atoms[32]

that the interaction strength between hybrid orbitals of rare gas atoms and Pu 7s, Pu 6p, Pu 6d and Pu 5f hybrid orbitals was not consistent, thus causing the electron density of states to change. The partial electron density of states adsorbed by different rare gases atoms on δ-Pu(100) surface is changed, as shown in Fig.14.

Many theories have been put forward by experimental researchers for a long time because the corrosion mechanism of plutonium in humid air is very complex. It is generally believed that plutonium reacts with water vapor to produce PuO_2 and H_2, and the reaction equation is $Pu(s)+2H_2O(g)\rightarrow PuO_2(s)+2H_2(g)$. Wei's research [42] showed that the adsorption between H_2O and Pu surface was very weak, and the total electron transfer was also few. The adsorption effect was determined by the interaction between H atom and Pu atom in the first layer. Li[46] studied the microscopic reaction mechanism of the interaction between gaseous plutonium and water, and obtained the corresponding reaction mechanism and topological properties.

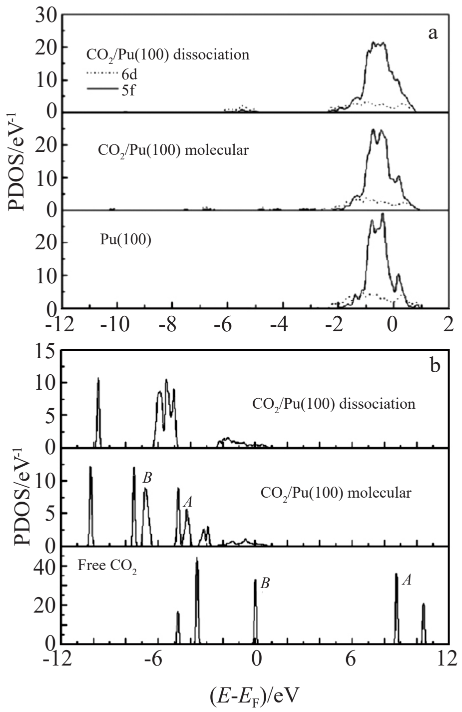

Fig.13 PDOS of CO_2 molecules (a) and Pu surface (b) before and after adsorption[36]

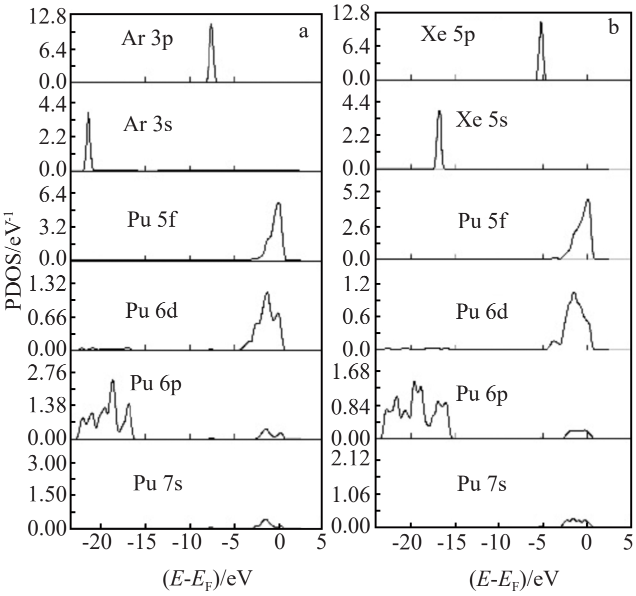

Fig.14 PDOS of rare gas atoms on Pu(100) surface[39]: (a) top position of Ar atom on δ-Pu(100) surface and (b) bridge site of Xe atom on δ-Pu(100) surface

5 Conclusion and Prospect

5.1 Main conclusions

1) The oxidation rate of plutonium in humid air is much faster than in dry air. In humid air, H_2 will cause the PuO_2 oxidation protection layer on the surface of plutonium to rupture and will also react with Pu to generate PuH with a fast reaction speed, causing the increase of corrosion rate of plutonium materials by thousands of times. Generally speaking, the higher the temperature, the faster the oxidation rate of plutonium.

2) The adsorption of H_2 and H_2O on different Pu surfaces belongs to physical adsorption, while the adsorption of O_2, CO and CO_2 on different Pu surfaces belongs to chemical adsorption, and mainly occurs at the first layer of Pu atoms on the surface; the more coordinated Pu atoms, the more stable the chemical bonding. C-down adsorption is more favorable than O-down when CO and CO_2 are adsorbed on different Pu surfaces. The adsorption of Xe atoms on Pu surface is chemical adsorption while the rest of rare gas are physical adsorption. Non-spin polarization and spin polarization have no effect on the optimal adsorption positions of various gases on different surfaces of Pu, but only affect the adsorption energy, Mulliken charge distribution and other relative parameters. The dissociation energy barriers vary for different gases, and O_2 has the highest dissociation energy barrier. Using different calculation models, methods and tools, the results are different.

3) The interactions of Pu with various active gases and rare gases are accompanied by charge transfer. The reaction mechanism is that the different hybrid orbitals of gas atoms and molecules interact with hybrid orbitals such as Pu7s, Pu6p, Pu6d, Pu5f to generate new chemical bonds, which leads to the generation of relative reactions and phenomena.

5.2 Research prospect

1) Improving research methods. In most researches, Dmol3 in Cerius2 and Materials Studio (4.1, 5.5), Gausssian03W software packages are used for modeling and calculating. We can also calculate by VASP software package, which uses ultra-soft pseudopotential and traditional self-consistent field cycle to calculate electronic ground state, to realize an effective, stable and fast self-consistent solution scheme of Kohn-Sham equation. We believe that better data and results will be obtained using VASP software package to calculate adsorption behavior of different gases on different Pu surfaces.

2) Studying the adsorption behavior of different surface of Pu atoms in different phases. We can study surface adsorption and dissociation behavior on different surfaces of Pu atoms in different phases, such as α-Pu(101), β-Pu(001), γ-Pu(010) and other surfaces, not limited to δ-Pu(100) and δ-Pu(111) and other surfaces, which will be more conducive to understanding and revealing the microscopic mechanism of Pu surface corrosion and the localization of its 5f electrons.

3) Exploring new systems to protect plutonium materials from oxidative corrosion. CO-H_2 system [30] enables a passive surface film to form on the compact and stable crystal surface of Pu_2O_3 to prevent the metallic plutonium from further corrosion by the inward diffusive CO and H_2 gas. So the effect of the CO_2-H_2 system, CO_2-H_2O system, CO_2-O_2 system, CO-H_2O system or other systems, and whether they can provide better protection for plutonium materials, which requires further research and analysis to obtain the best system to protect plutonium materials from oxidative corrosion.

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钚及其化合物表面腐蚀的研究进展

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摘　要：为了解掌握钚（Pu）及其化合物表面氧化腐蚀机理和探索能够有效缓解钚材料氧化腐蚀的环境体系，对国内外开展钚及其化合物表面化学的研究进行了综述，加深了对钚及其化合物在空气中的腐蚀行为的认识；对H_2、O_2、CO、CO_2等活性气体和Xe等稀有气体在钚及其化合物不同表面的吸附行为进行了对比分析，得到一些有益的结论。研究表明，Pu与各种活性气体和稀有气体的相互作用中伴随着电荷的转移，作用机理主要是气体原子分子的不同杂化轨道和Pu7s、Pu6p、Pu6d、Pu5f等杂化轨道相互作用生成了新的化学键，从而导致了相关反应和现象的产生。本研究还从改善研究方法、开展不同相的钚原子的不同表面吸附行为研究和探索防护钚材料氧化腐蚀新体系3个方面对钚及其化合物表面腐蚀研究工作进行了展望。

关键词：钚表面；活性气体；密度泛函；电子密度；吸附行为；作用机理

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