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Ab initio study of H/O trapping and clustering on U/Al interface*

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Al coating on U surfaces is one of the methods to protect U against environmental corrosion. The behaviors of hydrogen and oxygen impurities near the Al/α-U interface have been studied in the density functional theory framework. It turns out that U vacancies tend to segregate to the interface with segregation energies of around 0.5–0.8 eV. The segregated U vacancy can act as a sink for H and O impurities, which is saturated when filled with 8 H or 6 O atoms, respectively. Moreover, the O impurities tend to stay in the Al layer while the H impurities prefer to diffuse into the U lattice, suggesting that the Al coating can play a significant role against oxidation but not against hydrogenation of U.

Keywords: interface, uranium, aluminum, density functional theory

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1. Introduction

Uranium (U) is one of the most fundamental nuclear fuels in the nuclear industry. Corrosion induced by hydrogen (H) and oxygen (O) has been proved to be a challenge for U storage. To protect U against environmental corrosion, surface protection techniques are being researched, among which coatings of aluminum (Al) on the U surface have been reported.[1–3] Al electroplating was utilized in procession of U fuel elements[4] in the early years, with other techniques such as magnetron sputtering introduced later. Lu *et al.*[5] investigated the impact of different bias voltages of magnetron sputtering on microstructures and residual stress of Al coatings. For the growth mechanism, Zhou *et al.*[6] reported that Al films expanded in an island growth mode when sputtered on a U substrate. Moreover, diffusion on the U/Al interface has also been studied and factors including doped elements and interfacial microstructures were found to play significant roles in diffusion behaviors.[7–9]

The first-principles calculations based on density functional theory (DFT) have been utilized to study the structures and properties of U and relevant subjects. The lattice constants, elastic constants, electronic structures, and optical properties for α and γ uranium were studied by Chen *et al.*[10] Moreover, Zhang *et al.*[11] investigated property variances under pressure up to 100 GPa for α, β, and γ uranium. Taylor *et al.*[12] showed that H adsorption into the bulk U was endothermic, with the square-pyramidal interstitial site as the most stable one, and later he demonstrated a periodic variation in the interactions between U and a series of impurity atoms [H–Ar].[13] It has also been suggested that O impurities in bulk U could stabilize intrinsic vacancies by diminishing the vacancy formation energy from 1.98 eV to 1.7 eV and 0.8 eV for substitutional and interstitial O, respectively.[14]

First-principles calculations have also been employed to study the interaction between Al coatings and U substrates. Nie *et al.*[15] reported that upon Al adsorption, the α-U (001) surface contracted by about 3% and that 5f electrons of U atoms on the surface became delocalized, resulting from their hybridization with 3p electrons of Al atoms. It was further observed that upon adsorption of Al atoms, the spin magnetic moments of U atoms in the first layer decreased obviously and a ferrimagnetic phase emerged, different from a ferromagnetic phase reported by the previous research on a bare α-U (001) surface.

To reveal whether Al coatings on U substrates can play an important role against oxidation and hydrogenation of U, first-principles calculations were performed to study the interaction between O/H impurities and U/Al interfaces in the present work. A supercell consisting of a U/Al bilayer and a vacuum slab was constructed. U vacancies and impurity interstitials (H, O) were introduced at different distances from the interface. Single point energies of relaxed configurations were calculated to discuss the interactions between the defects and the interfaces. Moreover, the largest numbers of impurities trapped in a U vacancy on the U/Al interface were also presented.

2. Methods

The Vienna *ab initio* simulation package (VASP) code[16] was utilized with projector augmented wave (PAW) methods for pseudopotential and the GGA approximation of Perdew *et al.* (PW91)[17] for the exchange and correlation functional. Scalar-relativistic modeling of the relativistic effects was included in the PAW-core contribution, which is believed to reasonably supply the leading relativistic correction to the electronic structure.[18] A basis set of plane wave functions up to

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a kinetic energy cut-off of 400 meV was chosen in valence wave function expansion. A k-point grid of $2\times2\times1$ was generated under the Monkhorst–Pack scheme. Convergence criteria for the electronic and ionic relaxations were 10^{-5} eV and 0.02 eV·Å^{-1}, respectively. The electron distribution was described by the Methfessel–Paxton scheme with sigma of 0.1. The conjugation gradient algorithm was chosen for supercell relaxation. The parameters above were tested to narrow error down to about 2 meV per atom.

Considering computation efficiency and periodic boundary conditions, we constructed a supercell consisting of a U/Al interface under an orientation match of $(001)_{\rm U} \parallel (001)_{\rm Al}$ and $[100]_{\rm U} \parallel [110]_{\rm Al}$. In interfacial matching, the structural units of $4a_0[100]_{\rm U}\times 2b_0[010]_{\rm U}$ and $2\sqrt{2}a_0[110]_{\rm Al}\times 2\sqrt{2}a_0[1\bar{1}0]_{\rm Al}$ were specifically chosen along the interfacial plane, which yields a mismatch of about 2.5%. Moreover, an appropriate lattice displacement parallel to the interface was also implemented to create a better fit on the interface. The atom arrangement near the interface is shown in Fig. 1. The initial interface distance and vacuum slab thickness were 2.6 Å and 15 Å, respectively. For either side of the interface, five layers of atoms were included to screen the effect of the vacuum slab.

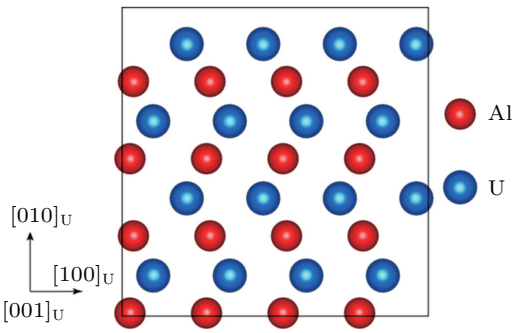


Fig. 1. (color online) Vertical view of atoms near the U/Al interface.

The initial supercell was relaxed with all freedoms to reduce effects of mismatch on the interface. Then vacancies and impurities were introduced around the interface zone and the atoms were further relaxed with supercell size and shape fixed. Single point energies were then calculated and compared.

Besides, the chemical potential of bulk U atoms and other reference data were also considered. For comparison with a previous research by Taylor,[13] a supercell of $(4a\times2b\times3c)$ α-U primitive cells was constructed, with PAW pseudopotential and GGA-PW91 functional utilized. A k-point grid of 4×4×3 was set by the Gamma scheme. The energy cutoff was 500 eV. The electronic distribution was determined by the Methfessel–Paxton scheme with sigma of 0.2. Convergence criteria for the electronic and ionic relaxations were 10^{-4} eV per atom and 0.05 eV·Å^{-1}, respectively. The supercell relaxation was implemented by the conjugate gradient algorithm. The calculated formation energies, $E_{\rm f}$, of U vacancy and H/O interstitials with reference to bulk U and a single H/O atom are given in Table 1. It can be seen that the $E_{\rm f}$ error of H is within 5%, while that of O is about 10%, which might be due to refinement of k-point sampling in the present research.

As U contains f valence electrons, the DFT+U method was often adopted in the DFT calculations. In our cases, we also conducted DFT+$U_{\rm eff}$ calculation for the U/Al interface with an appropriate $U_{\rm eff}$, and found that the results with the addition of $U_{\rm eff}$ are very close to those without $U_{\rm eff}$. For simplicity, only the first-principles calculations without $U_{\rm eff}$ are given in the present study.

Table 1. The formation energy of intrinsic vacancies, hydrogen interstitials, and oxygen interstitials in bulk U. Results from early reports are also listed.

$E_{\rm f}$/eV	Present work	Early reports
Vacancy	1.802	1.69–1.98[a]
H	–1.96	–1.91[b]
O	–5.9	–5.3[c]

[a]Refs. [14] and [19]; [b]Ref. [12]; [c]Ref. [13].

3. Results and discussion

3.1. Vacancy and interface interaction

The formation energies of vacancy ($E_{\rm f}$[V]) near the U/Al interface are defined as

$$E_{\rm f}[{\rm V}] = E_{\rm tot}[{\rm V}] - E_{\rm tot}[{\rm s}] + \mu_{\rm U}, \tag{1}$$

where $E_{\rm tot}$[V] and $E_{\rm tot}$[s] denote the total energies of the bilayer configuration with and without vacancies, and $\mu_{\rm U}$ is the chemical potential of bulk α-uranium atom.

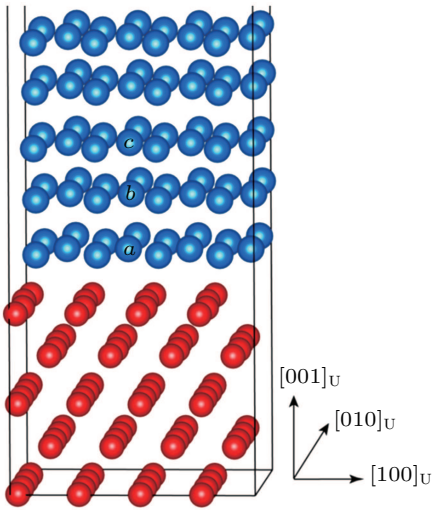


Fig. 2. (color online) Three U vacancy sites at the first, the second, and the third layers away from the U/Al interface are marked as a, b, and c, respectively.

Three U vacancy sites located at the first, the second, and the third layers away from the U/Al interface as shown in Fig. 2 are considered and the results are given in Fig. 3. It can be seen that $E_{\rm f}$[V] of U vacancy decreases by 0.55 eV and then increases slightly when the vacancy approaches the U/Al

interface from the third layer, suggesting that the vacancies tend to segregate at the interface. It is also noted that $E_f[V]$ of the vacancy at the third layer is comparable to that in the bulk U. It should be pointed out that the energy difference between vacancies at the first and the second layers away from the interface is negligible, as it is comparable to the error in calculations of single point energy. It is well known that the transmutations of uranium will generate considerable residual defects, so the above results suggest that the U/Al interface may play a significant role in the evolution of a defect structure, as it can act as a sink of vacancies.

Besides, we also consider the tendency whether the U vacancy on the U/Al interface would be occupied by the nearest Al atom, leaving a vacancy at the Al layer next to the interface. Our calculation shows that the deviation of the total energy is within 1 meV per atom, indicating no bias toward either of the structures. However, our research focuses on the impurity trapping effect of vacancies on the U side, because the number of vacancies on the U side is greater than that on Al coatings. This arises from two facts that the volume fraction of Al coatings to bulk U is small, resulting in fission neutron-generated vacancies in Al coatings smaller than that in bulk U and that the defects created by recoiled transmutation nuclei are mainly in the U side. As the vacancies are the typical sinks for corrosion elements and U vacancies tend to segregate to the U/Al interface, based on the above consideration, our goal is to give an upper limit of impurities (H or O) trapped by a single U vacancy at the interface. Thus only a configuration with a single U vacancy on the interface is used as the basis structure for consideration of the interaction between the interfacial vacancy and H/O impurities discussed below.

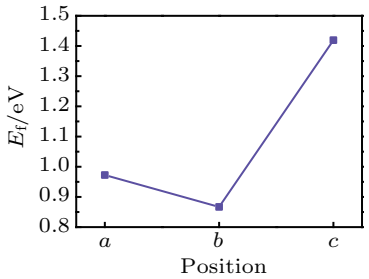


Fig. 3. (color online) Variation of the vacancy formation energy with distance away from the U/Al interface.

3.2. Interaction between H/O impurity and U/Al interface

A total of six interstitial sites for impurity atoms I (I = H, O) near the U/Al interface are considered in the research, which are displayed in Fig. 4. The calculation results of interface structures with and without a vacancy at site a in Fig. 2 are compared to reveal the role of the interfacial vacancies in trapping impurities.

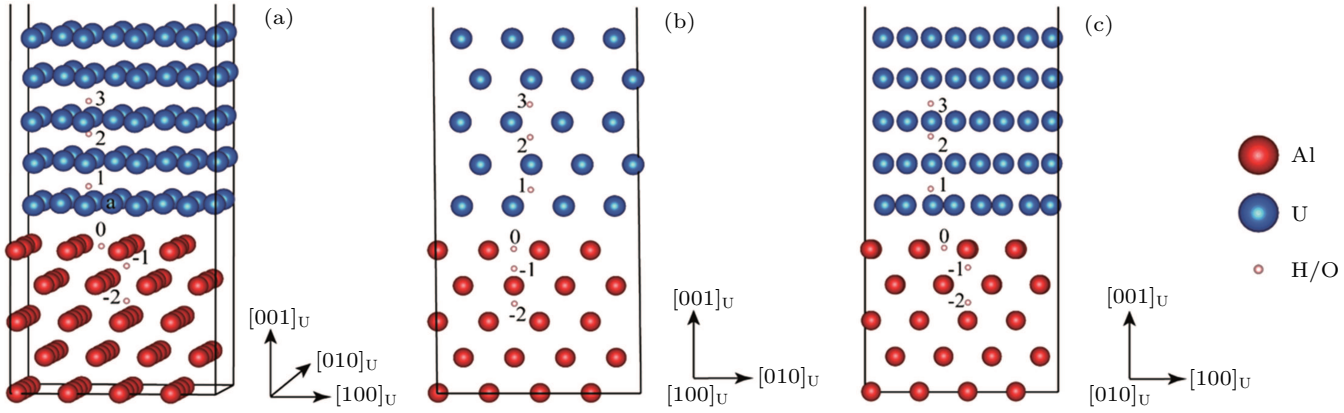


Fig. 4. (color online) Different views for the positions of interstitial impurities near the U/Al interface. Interstitial sites are indicated by integers from −2 to 0 at Al layers and from 1 to 3 at U layers.

To show clearly the energy variation with the different interstitial sites, the single point energy of No. −2 interstitial site is chosen as the reference state, which gives the energy deviation (ΔE) as follows:

$$\Delta E = E_{\text{tot}}[n] - E_{\text{tot}}[-2], \quad n = -1, 0, 1, 2, 3, \tag{2}$$

where n denotes the interstitial sites in Fig. 4.

The variation of the system energy with different impurity sites for H and O is calculated and given in Fig. 5. It can be seen from Fig. 5(a) that for the perfect U/Al interface, the total system energy with H impurity at U layers is lower than that at Al layers, indicating that the H impurities prefer to stay in the U lattice. Meanwhile, it can also be seen that the trap effect at the U/Al interface is sharply enhanced with the interface vacancy present, suggesting that the interfacial vacancies act as a H impurity sink. It can be seen from Fig. 5(b) that, contrary to H behavior, the system energy slowly increases with O impurity diffusing from the Al lattice toward the interface, then abruptly rises with O jumping to the U layer, and finally increases gradually with O moving into the U bulk, indicating that the O impurities tend to stay in the Al lattice. The interfacial vacancies can also be seen as a sink of O impurities, indicating the fact that the trapping effect appears only with the vacancy present at the interface. The above results sug-

gest that Al coatings on U can play an important role against U oxidation but not hydrogenation.

Moreover, we find that the H impurity is nearly stable at the sites shown in Fig. 4, as no obvious displacement occurs after relaxation. But it is noteworthy that under both conditions, the O interstitial atom located at the No. 0 site drifts back into the No. −1 site during relaxation. The trap effect also arises only when the interface vacancy is introduced.

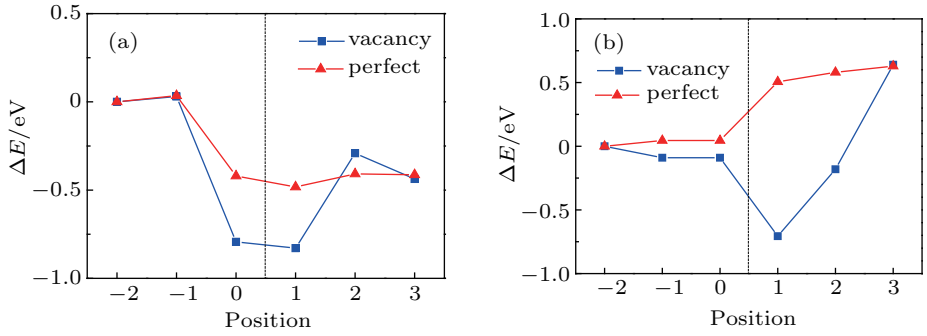


Fig. 5. (color online) Variation of the total energy with impurity sites for (a) hydrogen interstitials and (b) oxygen interstitials. The U/Al interface is indicated by the dash vertical line.

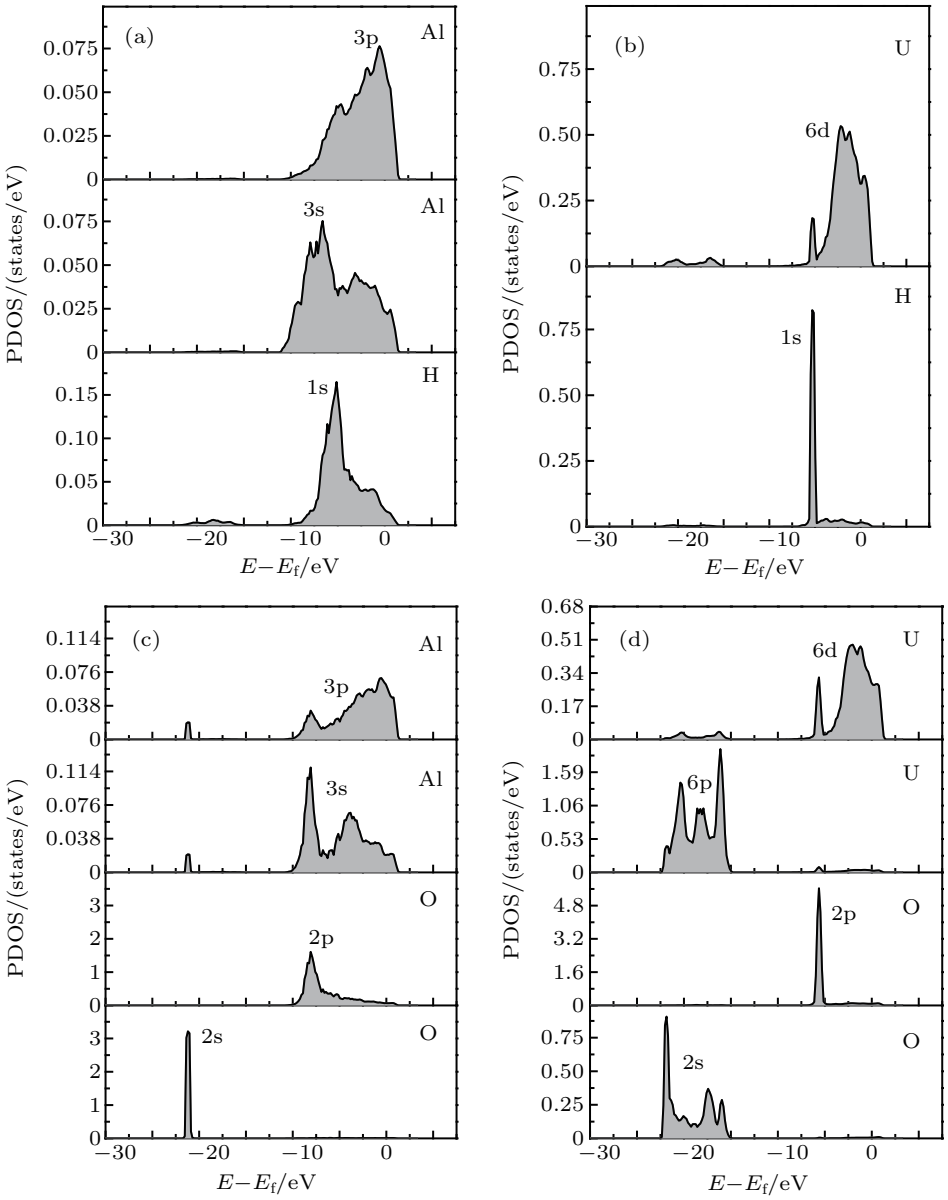


Fig. 6. Partial density of states (PDOS) of impurities and their nearest bulk atoms: H at (a) No. 0 and (b) No. 1 sites, O at (c) No. 0 and (d) No. 1 sites. A U vacancy has been introduced on the interface and only electron orbitals involved in the hybridization are shown here. Element types are marked on the upper right corner of subplots and orbital types near patterns.

To give a better insight into the nature of interactions between the impurities and the interface, an analysis of the partial density of states (PDOS) is performed. For simplicity, only interstitial sites closest to the U/Al interface (namely, No. 0 and No. 1 sites in Fig. 4) are analyzed and the results are given in Fig. 6. Only PDOS under the presence of a U vacancy on the interface is shown because no particular influence of the interfacial vacancy is found. For H at the No. 0 site, the PDOS pattern of the 1s orbital spreads as a broad continuum, indicating complex interactions with atoms nearby, which actually involves the 3s and 3p orbitals of Al at the same time. In contrast, sharp peaks are shown for H at the No. 1 site, with only the 6d orbital of U involved in hybridization. As for O, the 2s orbital shows little hybridization in Al, but resonates evidently with the 6p orbital of U. Meanwhile, the 2p orbital of O interacts with the 3s and 3p orbitals of Al and the 6d orbital of U. Although the hybridization patterns of impurities differ largely between the interfacial sites, they are actually similar to those in the corresponding pure metals, indicating that an impurity's hybridization mainly depends on its interaction with the neighbor atoms. It should be pointed out that no observable displacements for the total DOS are found for the impurity configurations with or without a U vacancy on the U/Al interface. Therefore, we may infer that the decrease of the system energy under the presence of a U vacancy at the interface is mainly attributed to lattice relaxation rather than the change of DOS structure.

3.3. Containment of impurities in interfacial vacancies

The capacity of a single U vacancy on the U/Al interface to adsorb H and O impurities is also discussed. The formation energy of a vacancy with n impurities adsorbed is defined as

$$E_{\mathrm{f}}^{n} = E_{\mathrm{tot}}[I_n\mathrm{V}] - E_{\mathrm{tot}}[\mathrm{V}] - n\mu_I, \quad I = \mathrm{H,O}, \tag{3}$$

where μ_I is the chemical potential of interstitials in bulk α-uranium. The binding energy (E_{b}) is also introduced for discussion, which is defined as

$$E_{\mathrm{b}}^{n} = E_{\mathrm{f}}^{n} - E_{\mathrm{f}}^{n-1}, \quad n = 1,2,3,\ldots \tag{4}$$

It could be seen that the intrinsic vacancy remains as an unfilled adsorption site when the binding energy is negative and it would be considered saturated with a positive binding energy. The final curve is plotted in Fig. 7. In particular, configurations with n impurities are set up by adding properly an extra impurity atom into the relaxed configuration with $n-1$ impurities. At last, a single U vacancy on the U/Al interface is found to be saturated with 8 H impurities. For the case of O impurities, the curve is truncated at 6 due to the fact that the next added O diffuses into the Al lattice, beyond the description of Eq. (4) and the interstitial cluster stops growing actually.

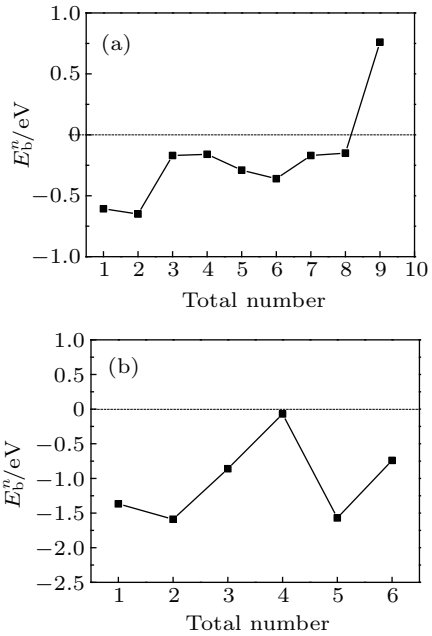


Fig. 7. Variations of binding energies with sizes of interstitial clusters of (a) hydrogen and (b) oxygen.

4. Conclusion

In the present research, the U/Al interface was demonstrated to be a crucial adsorption position for vacancies in the U lattice, with energy difference amounting to 0.5 eV. In general, H impurities tend to converge in the U lattice while O impurities in the Al lattice, indicating a more robust role of Al coating against oxidation than against hydrogenation in protection of U. Under a relative compact atomic arrangement without vacancies, no obvious trap effect was shown for H and O interstitials on the U/Al interface. However, with a single U vacancy introduced, the interface exhibited an evident trap effect for H and O interstitials. Moreover, single U vacancies were estimated to be capable of containing clusters of at most 8 H or 6 O impurities. In general, the U/Al interface exists as a sink adsorbing vacancies and impurities from the lattice which threaten the mechanical properties of the coatings.

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