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## A theoretical investigation and synthesis of layered ternary carbide system U-Al-C

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### ABSTRACT

This article presents the theoretical predictions and experimental synthesis of the uranium-containing layered ternary carbides  $UAl_3C_3$  and  $U_2Al_3C_4$ . The electronic structures and mechanical properties of  $UAl_3C_3$  and  $U_2Al_3C_4$  have been investigated by first-principles computations. The chemical bonding characteristics of  $UAl_3C_3$  and  $U_2Al_3C_4$  have been compared to those of nanolaminated ternary carbides and strong interactions have been found between uranium and carbon atoms. Furthermore,  $UAl_3C_3$  and  $U_2Al_3C_4$  powders have been fabricated by the solid state reaction method and the crystal structures of  $UAl_3C_3$  and  $U_2Al_3C_4$  have been determined by X-ray diffraction (XRD). Based on the present results, the layered ternary carbides  $UAl_3C_3$  and  $U_2Al_3C_4$  may provide an expansion of the derivative MAX phase (layered compounds) family as well as a new option for nuclear fuels.

### 1. Introduction

Nuclear power has been proven to be an environmentally friendly and cost-effective resource for large-scale electricity production. In pace with the continuing technological progresses in nuclear science, however, the top priority in the nuclear industry has always been the operational safety under normal conditions as well as in accidents since the March 2011 disaster at Fukushima, Japan. In that accident, which has a serious impact on public cognition to nuclear power, hydrogen explosions and the release of radionuclides were caused by the severe damage of the conventional  $UO_2$ -Zircaloy system during the loss of coolant accident (LOCA) scenarios [1]. As a consequence, the concept of ATFs (accident tolerant fuel system) was proposed shortly afterwards and has now become a major objective of research in nuclear industry worldwide [2–4]. Generally speaking, nuclear materials for the ATFs, including fuel pellets and claddings, are designed to prevent or delay the release of radionuclides or explosives during an accident event. Given that materials in a nuclear reactor inevitably suffer from an exceptionally harsh environment in combination of high temperature, high pressure, strong corrosion by coolants, intense radiation fluxes etc., the exploration of satisfactory ATF materials is still a challenge as

well as a new opportunity for materials science nowadays.

Recently, MAX phases, i.e. the ternary carbides and nitrides with the general formula  $M_{n+1}AX_n$  (where M is early transition elements, A is an A group element and X is C and/or N,  $n = 1, 2, 3$ ) have attracted tremendous attention due to their extraordinary mechanical, physical and chemical properties.  $Ti_3AlC_2$ ,  $Ti_2AlC$  and  $Cr_2AlC$  are typical examples of MAX phases [5], and some members exhibit better oxidation resistance and damage tolerance than refractory binary transition metal carbides, such as TiC, NbC, ZrC and HfC [6]. According to literatures, over 70 phases [7–14] have been successfully synthesized in bulk or thin film form by different combinations of M, A, and X elements since the discovery of MAX phases in the 1960's by Nowotny et al. [15]. Up to now, efforts are still being endeavored in the application of MAX phases as nuclear structural materials and the characterization of their behaviors under irradiation is still on the way [16–21].

In the past few years, along with the vigorous advance towards developing new MAX phase materials, a different family of layered ternary and quaternary compounds with the general formula of  $(TC)_nAl_3C_2$  and  $(TC)_n[Al(Si)]_4C_3$  (where T is metal atom,  $n = 1, 2, 3, \dots$ ) have also been discovered, such as the Zr-Al(Si)-C and Hf-Al(Si)-C systems [22–25]. Compared to the conventional MAX phases, the

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crystal structures of  $(\text{TC})_n\text{Al}_3\text{C}_2$  and  $(\text{TC})_n[\text{Al}(\text{Si})]_4\text{C}_3$  compounds can be described as  $\text{ZrC}_x$  or  $\text{HfC}_x$  blocks being interleaved by  $\text{Al}_3\text{C}_2$  or  $[\text{Al}(\text{Si})_4\text{C}_3]$  unit, which thus can be categorized as the derivatives of MAX phases (*d*-MAX). These  $(\text{TC})_n\text{Al}_3\text{C}_2$  and  $(\text{TC})_n[\text{Al}(\text{Si})]_4\text{C}_3$  materials display excellent mechanical and high temperature oxidation resistance properties as well as good manufacturability, which may render them candidate materials for high-temperature applications in advanced nuclear reactors. Furthermore, inspired by the recent progresses of the Zr-Al-C and Hf-Al-C systems [6] and the oxidation resistance of the MAX phase [26,27], one can envisage that the layered U-Al-C compound formed by incorporating Al into uranium carbide, which is traditionally used as fuel kernels for the US version of pebble bed reactors [28], might inherit the oxidation resistance and damage tolerance in the extreme conditions, and provide novel option for potential nuclear fuel in ATFs. To the best of our knowledge, little is yet known on the U-Al-C system to date. On these grounds, exploring the structure and fabrication technique of the U-Al-C system becomes important for the design of new nuclear fuel system and is interesting for the expansion of the MAX phase family.

In this work, we have investigated different phases of the U-Al-C system from the first principles method. The results suggested that  $\text{UAl}_3\text{C}_3$  and  $\text{U}_2\text{Al}_3\text{C}_4$  structures are probably dynamically stable. To verify these predictions, we have prepared  $\text{UAl}_3\text{C}_3$  and  $\text{U}_2\text{Al}_3\text{C}_4$  powders by the solid state reaction method and the effect of the synthesis temperature on the formation of  $\text{UAl}_3\text{C}_3$  and  $\text{U}_2\text{Al}_3\text{C}_4$  phases has been analyzed. Accordingly, characterizations of the crystallographic phases in the fabricated samples and the micromorphology of as-synthesized powders have been performed by X-ray diffractometry and scanning electron microscope.

## 2. Computational details

The crystalline structures and electronic properties of the U-Al-C compounds are determined based on density functional theory (DFT) as implemented in the software of Vienna Ab initio Simulation Package (VASP) [29]. The generalized gradient approximation (GGA) of the Perdue-Burke-Ernzerhof (PBE) [30] scheme is adopted for the correlation effects and exchange-correlation functional. The projected augmented wave (PAW) approach is employed for pseudopotentials; the plan-wave cutoff energy is chosen to be 550 eV. The conjugate gradient method is applied for structural optimization, and the system is relaxed until the force on each atom is less than  $1.0 \times 10^{-6}$  eV/atom. Moreover, all of the structures are visualized using the Materials Studio Visualizer [31].

## 3. Experimental details

The raw materials used in this study are UC (UC was self-prepared by solid phase reaction method with uranium dioxide and carbon as raw materials. Uranium dioxide and carbon were mixed for 24 h with the ratio of 1:3.1 mol in a polythene bottle using ethanol and  $\text{ZrO}_2$  balls and then dry pressed into disks. After that, the disk was sintered at 1500 °C for 2 h by pressureless sintering with Ar atmosphere.), aluminum (Al, Aladdin, China), and carbon (C, Degussa, Germany), with purities of 95%, 99%, and 99%, respectively. The starting mixtures of UC, aluminum and carbon are mixed for 24 h in a polythene bottle using ethanol and  $\text{ZrO}_2$  balls, and dried by bake oven. After being dried, the powder mixtures are dry pressed into disks (about 10 mm diameter and 3 mm thickness). Then the disks are calcined in a tube furnace at the desired temperature for 120 min under Ar atmosphere at a heating rate of 10 °C/min by solid state reaction. The densification processes of the synthesized  $\text{UAl}_3\text{C}_3$  powder are performed by pressureless sintering in temperature range of 1200–1400 °C for 2 h.

XRD patterns of the powders are collected by powder X-ray diffraction (XRD, Bruker AXS D8 Discover, Germany) experiments, using Cu K $\alpha$  radiation. Diffraction patterns are recorded using Cu K $\alpha$

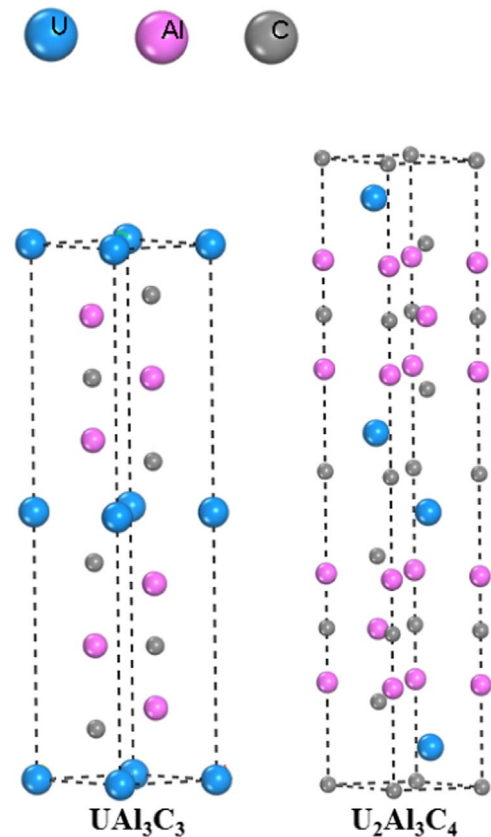


Fig. 1. Crystal structures of  $\text{UAl}_3\text{C}_3$  and  $\text{U}_2\text{Al}_3\text{C}_4$ .

radiation with  $2\theta$  from 10° to 90° in steps of 0.01° and a collection time of 10 s per step. The microstructures of the as-synthesized powders are characterized by scanning electron microscopy (SEM, Hitachi S-4800, Japan).

## 4. Results and discussion

In this work, the optimized structures for  $\text{UAl}_3\text{C}_3$  and  $\text{U}_2\text{Al}_3\text{C}_4$  are shown in Fig. 1. As aforementioned, the structures are both featured by the layered stacking, which are composed of  $(\text{UC})_n$  and  $\text{Al}_3\text{C}_2$ . The corresponding space groups and lattice parameters are shown in Table 1. For the  $\text{UAl}_3\text{C}_3$  phase, the calculated lattice parameters  $a$  and  $c$  are 3.381 Å and 17.41 Å, respectively, which are in excellent agreement with the previous measurement [25], demonstrating the reliability of the computational methods. As to the  $\text{U}_2\text{Al}_3\text{C}_4$  phase, the  $a$  value is approximately the same as that of  $\text{UAl}_3\text{C}_3$  but the  $c$  parameter rises to 23.31 Å. Comparing to the  $\text{Zr}_2\text{Al}_3\text{C}_4$  and  $\text{Hf}_2\text{Al}_3\text{C}_4$  phases, the  $\text{U}_2\text{Al}_3\text{C}_4$  phase manifests an expanding effect to the lattice due to the larger size of uranium atoms. Interestingly, the bond distances of U–C are 2.55 Å and 2.45 Å in  $\text{UAl}_3\text{C}_3$  and  $\text{U}_2\text{Al}_3\text{C}_4$ , respectively, which are close to that in UC [32] and shorter than that in  $\text{U}_2\text{C}_3$  [33], indicating that the formation of *d*-MAX phases maintains the strength of the U–C bonds.

To explore the stability of U-Al-C structures, we calculate their phonon spectra using the Phonopy codes [34] in combination with density functional perturbation theory in VASP. Fig. 2(a) and Fig. 2(b)

Table 1  
The calculated structural parameters ( $a$ ,  $c$ ) for  $\text{UAl}_3\text{C}_3$  and  $\text{U}_2\text{Al}_3\text{C}_4$ .

	$a$ (Å)	$c$ (Å)	Space group	
$\text{UAl}_3\text{C}_3$	3.381	17.41	$P63/mmc$	This work
$\text{UAl}_3\text{C}_3$	3.387	17.39	$P63mc$	Ref. [25]
$\text{U}_2\text{Al}_3\text{C}_4$	3.397	23.31	$P63/mmc$	This work

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