Progress in Nuclear Energy 99 (2017) 110–118

Contents lists available at ScienceDirect

Progress in Nuclear Energy

journal homepage: www.elsevier.com/locate/pnucene

Mechanical, electronic and thermodynamic properties of hexagonal and orthorhombic U_2Mo: A first-principle calculation

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ARTICLE INFO

Article history:
Received 15 June 2016
Received in revised form
3 April 2017
Accepted 15 May 2017

Keywords:
U_2Mo
Elastic properties
Phonon dispersion relations
Stress-strain relations
Density functional theory

ABSTRACT

First-principle investigations are presented based on density functional approach to calculate the elastic properties, stress-strain relations, phonon dispersion relations, electronic properties and thermodynamic properties of hexagonal and orthorhombic U_2Mo. The calculated energies in the present work suggest that hexagonal structure is more stable than orthorhombic one. The obtained elastic constants and moduli show that both phases of U_2Mo are ductile and elastically stable. Besides, the stress-strain relations and the corresponding theoretical tensile strengths of these two phases exhibit strong anisotropy in selected crystalline directions. The generated phonon dispersion curves without imaginary phonon mode imply these two compounds are dynamically stable. The analyzed results of the electrical properties demonstrate the electronic stability, and the hybridizations between the *f*-states of U and the *d*-states of Mo can be noted from derived band structures and partial densities of states for these two structures. Gibbs free energy and other thermodynamics quantities are also obtained and discussed in this paper.

1. Introduction

Uranium is the main component in nuclear fuel. Pure uranium exhibits three allotropic phases: a low-temperature orthorhombic α-phase (space group Cmcm), a high-temperature tetragonal β-phase (space group $P4_2/mmm$) and a higher temperatures body-centered cubic γ-phase (space group $Im\bar{3}m$) (Rechtien and Nelson, 1973). The α-U has a number of disadvantages that make it unacceptable for use as nuclear reactor fuel, such as poor oxidation and corrosion resistance, low hardness and yield strength. One of the effective and useful ways is to make uranium alloyed with other elemental metals (from groups V to VIII). Up to now, several elements such as Mo, Nb, Ti, and Zr have been proved to exhibit high degree of solid solubility in γ-U at high temperature (Tupper et al., 2012). Among them, U-Mo alloys have been regarded as the most prominent candidates because of their more stable irradiation performance compared with other high density uranium alloys and compounds.

Many researchers (Van Thyne and McPherson, 1957; Tangri and Williams, 1961; Craik et al., 1962; Howlett, 1970; Dabush et al., 2002; Burkes et al., 2009; Pedrosa et al., 2015) have carried out metallographic investigations of U-Mo system, and the thermodynamic properties for various U-Mo alloys ((Burkes et al., 2010a, 2010b; Kutty et al., 2012) were also experimentally investigated. It was found that Mo exhibits a high solubility (*ca.*35 *at.*%) in bcc γ-U at high temperature, but below 833 K the equilibrium state becomes a mixture of α-U and the intermetallic compound U_2Mo (Rough and Bauer, 1958). Experimental measurements have already revealed that the synthesized U_2Mo is a $MoSi_2$ type compound having a $C11_b$ structure (space group I4/mmm). The phase transformation from U_2Mo to bcc γ-phase was also observed at 853 K (Kutty et al., 2012). In fact, the U_2Mo compound is a compromise between high fissile material density and stable behavior.

For years, many theoretical results on U-based alloys have been reported (Alonso and Rubiolo, 2007; Landa et al., 2011; Jaroszewicz et al., 2013; Wang et al., 2014; Liu et al., 2015; Losada and Garcés, 2015, 2016). Alonso and Rubiolo (2007) firstly evaluated the thermodynamic functions of U-Mo systems employing the first principle calculations. Landa et al. (2011) studied the ground-state properties of U-Mo solid solutions by density functional theory.

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http://dx.doi.org/10.1016/j.pnucene.2017.05.012
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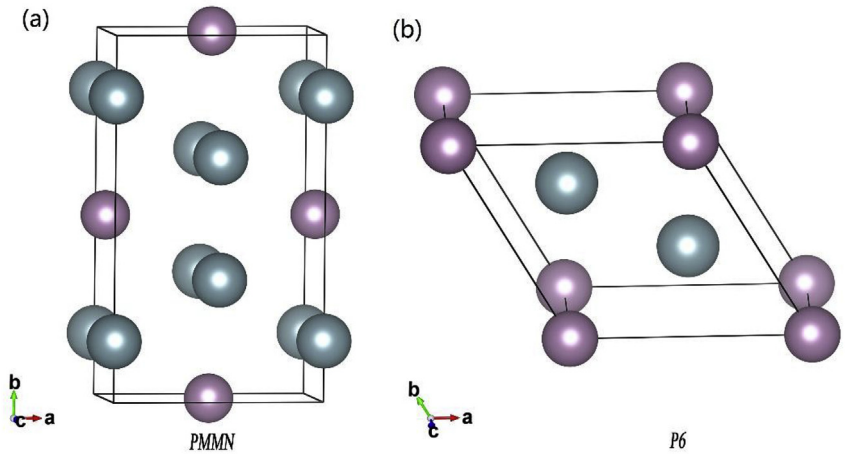

Fig. 1. The structure of U_2Mo: (a) orthorhombic (Pmmn) phase; (b) hexagonal (P6) phase. The purple and light blue circles are Mo and U atoms, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 1
The optimized structural parameters (lattice constant in Å, the atomic positions).

	a	b	c	U	Mo	References
Pmmn	4.831	8.315	2.720	(0,0.167,1.0)	(0,0.5,0.5)	Wang et al. (2014)
Pmmn	4.817	8.342	2.740	(0,0.167, 1.0)	(0,0.5,0.5)	This work
P6	4.821	4.821	2.773	(0.333, 0.667,0.5)	(0,0,0)	Losada and Garcés (2016)
P6	4.818	4.818	2.738	(0.333, 0.667,0.5)	(0,0,0)	This work

Table 2
Calculated elastic constants (in GPa), bulk modulus B, shear modulus G, B/G, Young's modulus Y and Poission's ratio υ of Pmmn and P6 phase of U_2Mo (all in GPa except for υ).

	C_{11}	C_{22}	C_{33}	C_{44}	C_{55}	C_{66}	C_{13}	References
Pmmn	299	293	246	74	73	87	116	Wang et al. (2014)
Pmmn	298.37	296.33	242.19	63.34	83.66	66.74	120.96	This work
P6	304	–	288	66	–	–	103	Losada and Garcés (2016)
P6	272.52	–	227.30	78.37	–	–	104.18	This work
	C_{12}	C_{23}	B	G	G/B	Y	υ	
Pmmn	131	133	198	91	0.46	238	0.30	Wang et al. (2014)
Pmmn	131.44	122.85	195.29	72.96	0.37	194.6	0.334	This work
P6	123	–	173	81	0.47	210	0.3	Losada and Garcés (2016)
P6	112.33	–	156.33	77.31	0.49	199.2	0.2877	This work

Jaroszewicz et al. (2013) calculated the mechanical and thermal properties with a conclusion that U_2Mo of $C11_b$ structure has structural stability. However, the consistent conclusion that I4/mmm structural U_2Mo is a mechanically and dynamically unstable phase has been obtained in recent years (Wang et al., 2014; Liu et al., 2015; Losada and Garcés, 2015). So, searching for a stable phase of U_2Mo attracted many researchers' attention. Wang et al. (2014) found a stable orthorhombic structure of U_2Mo (space group Pmmn) by first principle calculations. More recently, a new ground-state of hexagonal U_2Mo (space group P6) was also found (Losada and Garcés, 2015). To date, there is no systematic study of mechanical, electronic and thermodynamic properties of these two structures, which are significantly important for experimental synthesis and practical application in the future. Thus, a theoretical predication of structural, mechanical and thermodynamic properties of orthorhombic and hexagonal U_2Mo is urgently needed.

Therefore, in this paper, we employ density-functional theory calculation to investigate the hexagonal and orthorhombic U_2Mo. The elastic properties, stress-strain relations, phonon dispersion relations, electrical properties and thermodynamic properties were taken into account and systematically calculated. The paper is organized as follows: Section 2 describes the computational details of this study. In Section 3, the theoretical properties of U_2Mo compound with two different phases are presented and discussed in detail. General conclusions in section 4 finalize the paper.

2. Computation method

In the present work, the first-principle calculations were carried out within density-functional theory (DFT), as implemented in Vienna Ab initio Simulation Package (VASP) code (Kresse and Hafner, 1993; Kresse and Furthmüller, 1996a, b). The plane-wave basis set was employed within the framework of the projector augmented wave (PAW) method (Blöchl, 1994; Kresse and Joubert, 1999). GGA calculations were employed using exchange-correlation functional parameterized by Perdew, Burke and Ernzerhof (PBE) (Perdew et al., 1996). The cutoff energy of 500 eV were used in all calculations and the *k*-point meshes in the Brillouin zone (BZ) were sampled by 11 × 11 × 11 for orthorhombic Pmmn structure and 11 × 11 × 13 for hexagonal P6 structure according to Monkhorst-Pack scheme. During structural optimization, the