Stable Properties of $NbAl_3$ under High Pressure: Theoretical Predictions and First-Principles Calculations

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Abstract. Nb-Al alloy compounds are expected to be high temperature structural materials. However, the low toughness and poor oxidation resistance are the main obstacles to hinder Nb-Al intermetallics from applications. In this paper, a new monoclinic phase of $NbAl_3$ was proposed by particle swarm optimization. Structural and mechanical properties of monoclinic phase were investigated using the first-principles method. The calculated enthalpies suggested that the known tetragonal structure was more stable than monoclinic structure from 0 to 200 GPa, but the ductility of monoclinic phase was better than that of tetragonal phase.

Introduction

With the development of high temperature structural materials, Nb-Al intermetallic compounds attract our attention because of their high melt point, low density and excellent high temperature strength [1-3]. Nb-Al intermetallics mainly include Nb_3Al, Nb_2Al and $NbAl_3$ [4]. Among them, $NbAl_3$ has a tetragonal structure [5]. Based on the Gibbs energy of formation, George et al. [6] found that $NbAl_3$ was the most stable compound in the Nb-Al system. To the best of our knowledge, many investigations have been carried out on $NbAl_3$ [7-12]. Xu et al. [10] found that the stability of $NbAl_3$ compound was depended on the covalent interactions between Al-p and transition-metal Nb-d states. Diffusion study [13] found that $NbAl_3$ had two intermediate phases: $TiAl_3$ type and cubic type. However, the low room temperature ductility and toughness due to complex crystal structure and less slip band, and the poor oxidation resistance of Nb-Al intermetallics lead to brittle fracture [14, 15]. Hence, many works have been performed to solve these problems.

Although $NbAl_3$ has the lowest oxidation rate among the Nb-Al system, the protective Al_2O_3 scales can't be formed on its surfaces [16]. Hebsur et al. [17] improved the high-temperature oxidation resistance of $NbAl_3$ by macroalloying with Cr, Y and Si. However, the fracture toughness of $NbAl_3$ was only 2.5 ± 0.5 $\mathrm{MPa}\sqrt{\mathrm{m}}$ [18]. The improvement of strength and low-temperature toughness of $NbAl_3$ is limited because of the large coefficient of thermal expansion (CTE) mismatch and chemical incompatibility between WHfC filaments and matrix [19]. Ray et al. [20] enhanced the strength of $NbAl_3$ by mixing 1% TiB_2. The oxidation resistance, high-temperature strength and brittle-to-ductile transition temperature (BDTT) could be controlled by changing the content of $NbAl_3$, NiAl and NbNiAl [21]. The high-temperature strength and BDTT decreased with the increase of Ni content, but the fracture toughness and oxidation resistance increased [22]. Although macroalloying, rapid solidification, grain refining and fabrication of composites can improve ductility and oxidation resistance for $NbAl_3$, these methods seem to be insufficient for

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industrial applications [23]. Hence, we expect to find a new structure with excellent performance for $NbAl_3$ by using CALYPSO code [24].

Computational Methods

Firstly, the local optimizations to predict stable or metastable phases were carried out using the Crystal structure AnaLYsis by Particle Swarm Optimization (CALYPSO) [24]. Secondly, the CASTEP package [25] was used to calculate the physical properties within generalized gradient approximation (GGA) and PW91 functional [26]. The energy cutoff 400 eV and the Monkhorst-Pack mesh [27] with 10×5×20 and 12×12×6 for monoclinic and tetragonal phases were used.

Results and Discussion

Two phases of $NbAl_3$ have been predicted: one is tetragonal and the other is monoclinic. Fig. 1 shows the crystal structures of tetragonal I4/mmm phase and monoclinic Cm phase. As far as we know, the most stable structure is I4/mmm phase. In order to compare with each other, the structural parameters of two phases are calculated [28], which are shown in Table 1. It can be seen that our calculated lattice constants of I4/mmm structure agree well with the published data. The ratio V/V_0 as a function of external pressure is plotted in Fig. 2, where V_0 is volume at T=0 and P=0. As the pressure increases from 0 to 200 GPa, the ratio of I4/mmm decreases more slowly than that of Cm. Moreover, the curves are smooth. Fig. 3 shows the enthalpies of monoclinic and tetragonal structures under pressure. In order to clearly distinguish whether there is a phase change, the enthalpy difference is drawn in subgraph. It is noted that the I4/mmm structure is more stable from 0-200 GPa. That is to say, no phase transition occurs at the pressure up to 200 GPa.

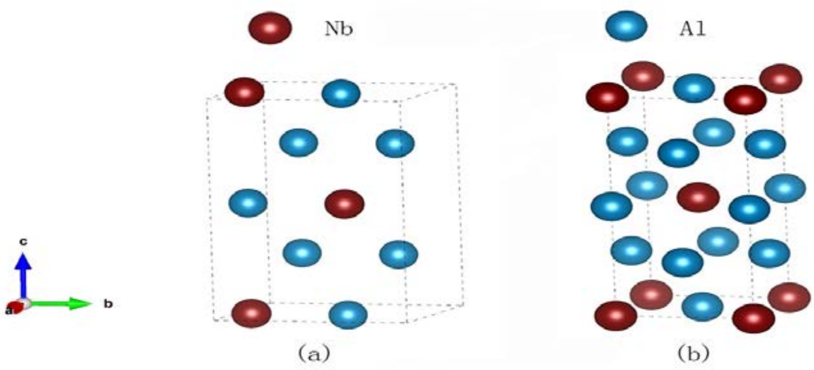

Fig. 1. The crystal structures of $NbAl_3$: (a) Cm, (b) I4/mmm.

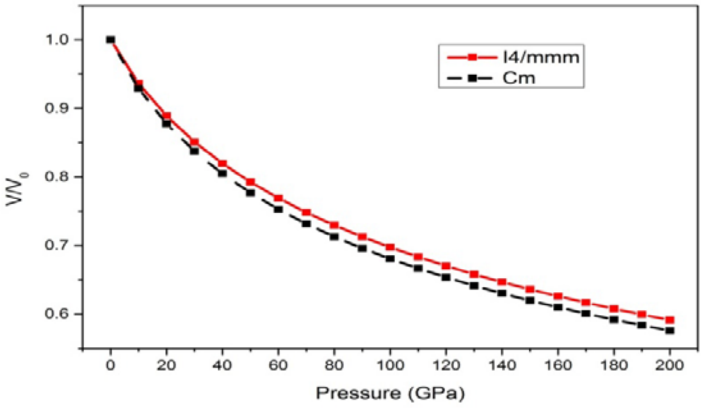

Fig. 2. The ratio of V/V_0 for $NbAl_3$.

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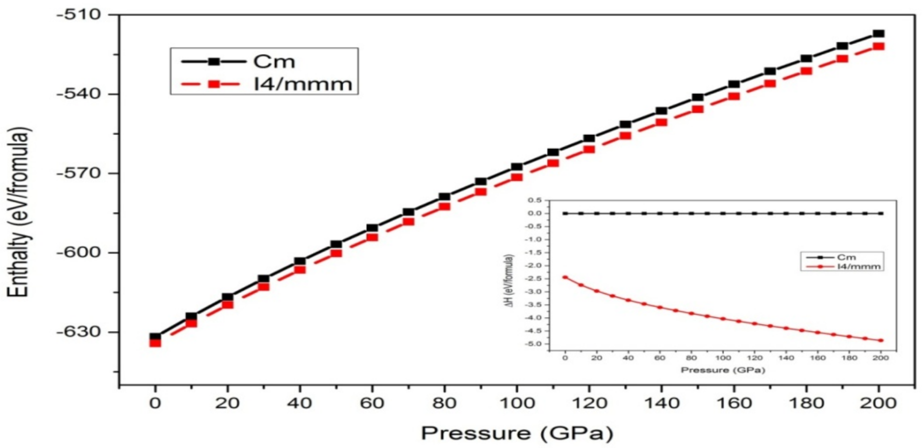

Fig. 3. The enthalpies of monoclinic structure and tetragonal structure $NbAl_3$ under pressure, and the relationship of enthalpy difference under pressure.

Table 1 Structural parameters of $NbAl_3$ under zero pressure

Space group	Structural parameters			
	a (Å)	*b* (Å)	*c* (Å)	*β* (°)
Cm	5.648	9.321	2.852	120.367
I4/mmm	3.805		8.590	
	3.844^a		8.605^a	
	3.841^b		8.614^b	
	$3.841{\pm}0.001^c$		$8.609{\pm}0.002^c$	
	3.845^d		8.601^d	
	3.83^e		8.57^e	
	3.801^f		8.538^f	
	3.803^g		8.602^g	

[a] Ref. [4]. [b] Ref. [7]. [c] Ref. [8]. [d] Ref. [9]. [e] Ref. [10]. [f] Ref. [11]. [g] Ref. [12].

Table 2 Elastic constants and bulk modulus in GPa of I4/mmm and Cm under zero pressure.

	C_{11}	C_{12}	C_{13}	C_{15}	C_{22}	C_{23}	C_{25}	C_{33}	C_{35}	C_{44}	C_{46}	C_{55}	C_{66}
I4/mmm	270	98	49					285		105			140
[11]	260.2	96.7	46.5					280.3		109.9			142.5
[12]	255.6	101.4	51.2					274.8		104			140.5
Cm	219	79	69	-25	250	52	5.9	261	4	58	3	85	70

	B	**B′**
I4/mmm	137.9	3.9
[12]	136	4
Cm	120.3	4

The independent elastic constants, bulk modulus and first pressure derivative of bulk modulus

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from Birch-Murnaghan EOS [29] are given in Table 2. It can be seen that our calculated elastic constants and bulk modulus of I4/mmm structure are in good compliance with the data [11,12]. The bulk modulus of I4/mmm structure is larger than that of Cm structure.

The Born stability criteria for tetragonal and monoclinic crystals are given in these equations [30-32]:

Tetragonal phase: $C_{11} > 0$, $C_{33} > 0$, $C_{44} > 0$, $C_{66} > 0$, $(C_{11} - C_{12}) > 0$, $(C_{11} + C_{33} - 2C_{13}) > 0$, $(2C_{11} + C_{33} + 2C_{12} + 4C_{13}) > 0$,

Monoclinic phase: $C_{11} > 0$, $C_{22} > 0$, $C_{33} > 0$, $C_{44} > 0$, $C_{55} > 0$, $C_{66} > 0$, $(C_{11} + C_{22} + C_{33} + 2C_{12} + 2C_{13} + 2C_{23}) > 0$, $(C_{33}C_{55} - C_{35}^2) > 0$, $(C_{44}C_{66} - C_{46}^2) > 0$, $(C_{22} + C_{33} - 2C_{23}) > 0$, $[C_{22}(C_{33}C_{55} - C_{35}^2) + 2C_{23}C_{25}C_{35} - C_{23}^2C_{55} - C_{25}^2C_{33}] > 0$,

$$
\begin{aligned}
&\{2[C_{15}C_{25}(C_{33}C_{12} - C_{13}C_{23}) + C_{15}C_{35}(C_{22}C_{13} - C_{12}C_{23}) \\
&+C_{25}C_{35}(C_{11}C_{23} - C_{12}C_{13})] - [C_{15}^2(C_{22}C_{33} - C_{23}^2) \\
&+C_{25}^2(C_{11}C_{33} - C_{13}^2) + C_{35}^2(C_{11}C_{22} - C_{12}^2)] \\
&+C_{55}(C_{11}C_{22}C_{33} - C_{11}C_{23}^2 - C_{22}C_{13}^2 - C_{33}C_{12}^2 + 2C_{12}C_{13}C_{23})\} > 0
\end{aligned}
\quad .
$$

It is evident that the elastic constants of two phases satisfy the mechanical stability criteria, meaning that two structures are mechanically stable at zero pressure.

The Pugh's ratio [33] (G/B) and Possion's ratio (ν) are used to determine the ductile/brittle behavior of intermetallics. The G/B ratio is greater than 0.57 or the ν is less than 0.26 [34], meaning that the material behaves in a brittle behavior. The calculated values of G/B ratio and ν of tetragonal structure are 0.82 and 0.177, suggesting that the tetragonal phase shows a brittle behavior. The values of G/B ratio and ν of monoclinic phase are 0.60 and 0.248, respectively. Although the monoclinic phase also shows a brittle behavior, this behavior is obvious weaker than that of tetragonal phase.

Conclusions

In summary, the paper has conducted a study of the structure, enthalpy, elastic and mechanical properties of $NbAl_3$ compound by combining first-principles calculations with particle swarm optimization. The pressure dependence of the enthalpy of $NbAl_3$ suggests that monoclinic (Cm) structure is less stable than tetragonal (I4/mmm) structure from 0 to 200 GPa. Besides, two structures are stable under zero pressure. Two phases all show brittle behavior at zero pressure. This provides a basis for subsequent work.

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