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First-principles study on the effect of Hf content on martensitic transformation temperature of TiNiHf alloy*

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In this paper a first-principles study of the electronic structure and stability of B2 $Ti_{1-x}NiHf_x$ ($x = 0.2, 0.4, 0.6$) and B19′ $Ti_{1-x}NiHf_x$($x = 0, 0.5$) alloys is presented. The calculations are performed by the plane-wave pseudopotential method in the framework of the density functional theory with the generalized gradient approximation. This paper calculates the lattice parameters, density of states, charge density, and heats of formation. The results show that the electronic structure and stability of B2 $Ti_{1-x}NiHf_x$ change gradually with Hf content. However, Hf content has little effect on the electronic structure and stability of B19′ $Ti_{1-x}NiHf_x$. The mechanism of the effect of Hf content on martensitic transformation temperature of TiNiHf alloys is studied from the electronic structure.

Keywords: DFT, TiNiHf, electronic structure, martensitic transformation temperature
PACC: 7115A, 7115M, 8130K

1. Introduction

In recent years, shape memory alloys (SMAs) have been widely used in the fields of engineering and medicine. Currently, robotic, automotive, aerospace industries and others need SMAs operating at temperature higher than 390 K. Consequently, seeking SMAs with a high martensitic transformation temperature (MTT) has attracted wide interest and attention. Nowadays, TiNiHf alloys are considered to be attractive candidates for SMAs used at high temperatures.[1,2] It has been experimentally found that the MTT of TiNiHf alloys increases considerably when Ti is replaced by Hf and the Hf content is above 8 at%.[3] In order to design the novel high-temperature SMAs, studies of the mechanism of high MTT in SMAs are important. Although much theoretical and experimental work has been devoted to investigate the mechanism of martensitic transformation in Ti-based binary SMAs,[4−8] researches on the mechanism of high MTT in TiNiHf alloys have not been reported yet. It is noted that there is a close relationship between the electronic structure and martensitic transformation.[9−11] Therefore, it is desirable to study the electronic structure and stability of TiNiHf alloys for pursuing the origin of their high MTT.

In this paper, we investigate the electronic structure and stability of B2 $Ti_{1-x}NiHf_x$ ($x = 0.2, 0.4, 0.6$) and B19′ $Ti_{1-x}NiHf_x$ ($x = 0, 0.5$) alloys by the first-principles method for understanding the mechanism of the effect of Hf content on their MTT. Computational methods are described in Section 2. The electronic structure and stability are analysed in Section 3. Conclusion is given in the last Section.

2. Method of calculation

The calculations presented in this study are performed with the Cambridge Serial Total Energy Package (CASTEP) code,[12] based on density functional theory, using Vanderbilt-type ultrasoft pseudopotentials[13] and a plane-wave expansion of the wave functions. We use the generalized gradient approximation (GGA) in the scheme of Perdew–Burke–Eruzerhof to describe the exchange and correlation potential. The structure is optimized with the Broyden–Fletcher–Goldfarb–Shanno method, and convergence is assumed when the forces on atoms are less than 0.03 eV/Å. The plane-wave cutoff energy of 340 eV is employed. The calculations are done by using a $(8, 8, 2)$ Monk horst-Pack grid. The initial crystal

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structures of the B2 $Ti_{1-x}NiHf_x$ with $x = 0.2, 0.4, 0.6$ are taken as a $(1 \times 1 \times 5)$ B2 TiNi supercell, in which appropriate Ti is replaced by Hf. The initial crystal structure of B19′ $Ti_{0.5}NiHf_{0.5}$ is obtained through replacing one Ti by Hf in the B19′ TiNi cell. The lattice constant of B2 TiNi supercell is taken from Ref.[14]. In the case of B19′ TiNi cell, we use the lattice parameters and atomic positions presented by Kudoh *et al.*[15] In every case, the geometrical optimization is always made, and it is used to calculate the lattice parameters, electronic structure and heats of formation are then calculated.

3. Results and discussion

The lattice parameters of B2 $Ti_{1-x}NiHf_x$ and B19′ $Ti_{1-x}NiHf_x$ after optimization are listed in Table 1 and Table 2 respectively. For the optimized B2 $Ti_{1-x}NiHf_x$ serials, the lattice constants are slightly smaller than the experimental values.[15] The maximum error is about 2 %, which is within the accuracy of GGA. The calculated lattice parameters of B19′ $Ti_{1-x}NiHf_x$ serials agree well with the experimental values.[16] These results demonstrate that the geometry and pseudopotentials used here are reliable.

Table 1. Calculated lattice constants a (nm) and heat of formation H (eV) of B2 $Ti_{1-x}NiHf_x$ $(x = 0, 0.2, 0.4, 0.6)$.

	$x = 0$	$x = 0.2$	$x = 0.4$	$x = 0.6$
a/nm	0.3016	0.3022	0.3069	0.3083
H/eV	0.63	0.55	0.49	0.38

Table 2. Calculated lattice parameters of B19′ $Ti_{1-x}NiHf_x$ $(x = 0, 0.5)$.

	a/nm	b/nm	c/nm	β/(°)
$x = 0$	0.2956	0.4040	0.4853	98.77
$x = 0.5$	0.3166	0.4082	0.4974	103.83

Figure 1 shows the calculated total density of states (DOS) and partial DOS for B2 $Ti_{1-x}NiHf_x$ serials and B2 TiNi. It is seen that the shape of total DOS for all looks similar. This is understandable because the addition of Hf does not change crystal structure of austenitic phase.

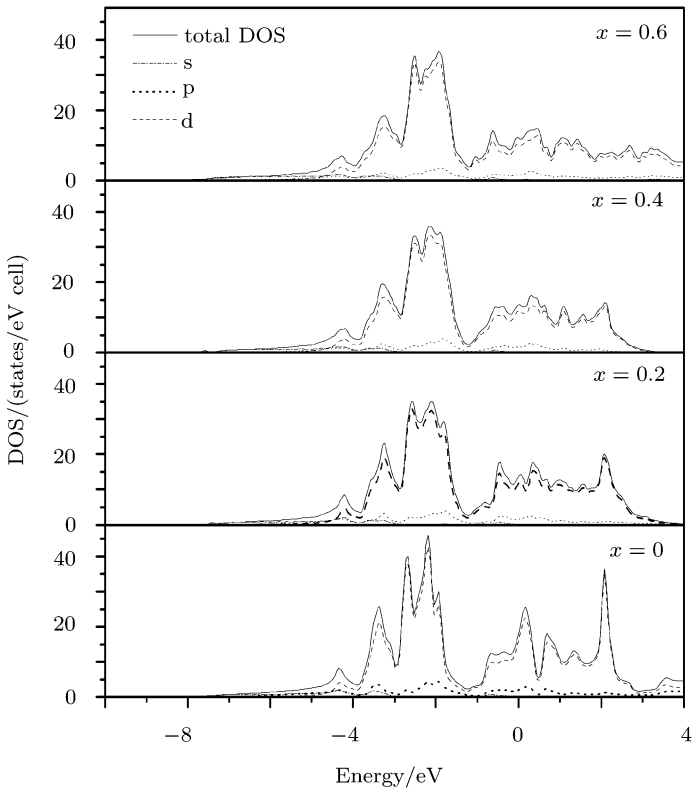


Fig.1. Total DOS and partial DOS of B2 $Ti_{1-x}NiHf_x$ $(x = 0, 0.2, 0.4, 0.6)$.

The total DOS resembles that of a bcc metal in the case that it consists of two sets of peaks separated by a dip. It can be found that the total DOS is mainly due to d states. There are negligible contributions from the p states and s states. For B2 TiNi, the Fermi level lies near a small dip in a rising part of the DOS below the higher energy peaks which are mostly unoccupied. This feature is consistent with the results in Ref.[6]. However, for the total DOS of B2 $Ti_{1-x}NiHf_x$ serials, a new small peak emerges near the Fermi level, and the position of this peak shifts towards the Fermi level with the increase of Hf content. As well known, when a Fermi level falls on the dip, corresponding structure is more stable than the one whose Fermi level does not fall on the dip.[4] Thus, B2 $Ti_{1-x}NiHf_x$ is unstable. Moreover, in the energy range from -3 eV to -2 eV, the sets of peaks of B2 TiNi have fine structure. But, those of B2 $Ti_{1-x}NiHf_x$ broaden due to Hf addition.

Figure 2 shows the total DOS of the B2 $Ti_{1-x}NiHf_x$ serials. Compared with B2 TiNi, the low energy peaks of B2 $Ti_{1-x}NiHf_x$ shift towards higher energies. The total DOS at Fermi level slightly decreases with the increase of Hf content. Another important feature in the total DOS of B2 $Ti_{1-x}NiHf_x$ lies in the pseudogap centred at about 1 eV below Fermi level. The pseudogap of B2 TiNi is the lowest and broadest among them. With the increase of Hf content, the pseudogap of B2 $Ti_{1-x}NiHf_x$ becomes gradually higher and narrower. The concept of a pseudogap has been much emphasized for intermetallics which states that a deeper pseudogap corresponds to a more stable structure of an intermetallic compound.[17] From this analysis, the increase of Hf content decreases the stability of B2 $Ti_{1-x}NiHf_x$.

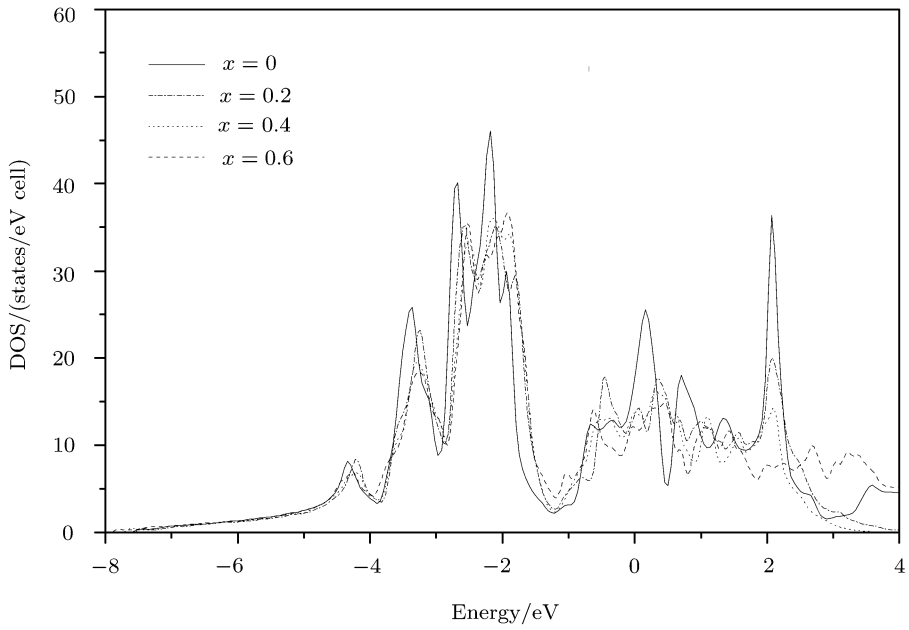


Fig.2. Comparison of total DOS of B2 $Ti_{1-x}NiHf_x$ ($x = 0, 0.2, 0.4, 0.6$).

As discussed above, the total DOS is mainly consisted of d states. We decompose the total DOS into site and angular momentum contributions. Figure 3 shows Ti d, Ni d and Hf d states for B2 $Ti_{1-x}NiHf_x$ serials and B2 TiNi. It can be seen that, the total DOS below Fermi level comes mainly from the Ni d states, and the total DOS above Fermi level is mainly due to the Ti d and Hf d states. There is a significant intensity for Ni site at the lower energies, and Ti and Hf site at the higher energies, indicating hybridization between the orbitals on the Ti (Hf) and Ni sites. Comparing Fig.1 with Fig.3, we find that the double peak structure mentioned above is produced by the hybridization between Ti (Hf) d and Ni d states. How-

ever, the peaks of Ti d states are higher than those of Hf d states, which implies that the hybridization between Hf d and Ni d states is weaker than that between Ti d and Ni d states. The narrowed pseudogap with the increase of Hf content is ascribed to this. In addition, with the increase of Hf content, there is a decrease of the bandwidth of Ni d states, signalling the weakened participation of the Ni d states in the hybridization.

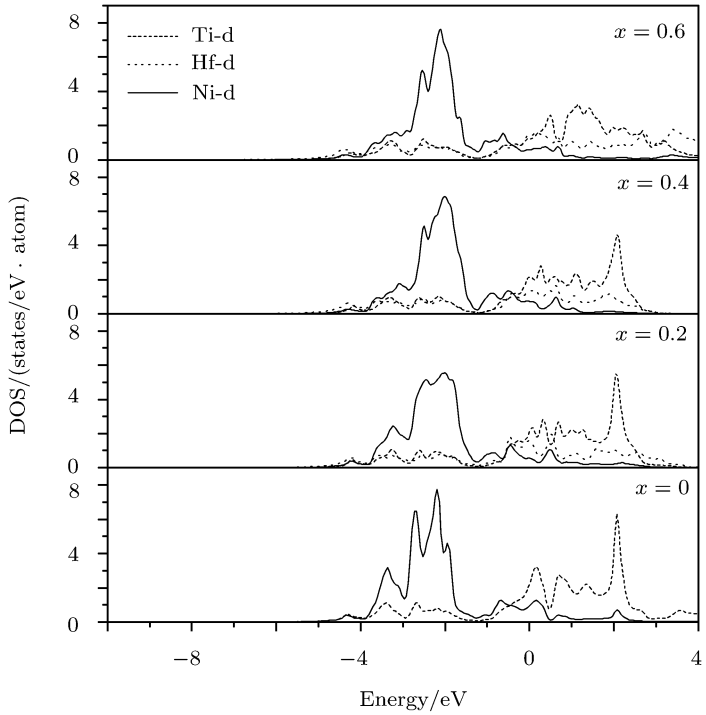


Fig.3. d partial DOS of B2 $Ti_{1-x}NiHf_x$ ($x = 0, 0.2, 0.4, 0.6$) for Ti, Hf and Ni site.

In order to know clearly the interaction between the Ti (Hf) atoms and Ni atoms in B2 $Ti_{1-x}NiHf_x$, we calculate their charge density. Figure 4 shows the charge density maps in the (110) plane of B2 $Ti_{1-x}NiHf_x$. As seen in this figure, there is the hybridization between the Ti (Hf) and Ni atoms. However, the charge density around Hf atoms is lower and more localized than that around Ti atoms. Therefore, the hybridization between Ti and Ni atoms is stronger than that between the Hf and Ni atoms which is consistent with the analysis of DOS.

It is well known that there is a correlation between phase stability and heat of formation. The calculated heats of formation of B2 $Ti_{1-x}NiHf_x$ are listed in Table 1. The heat of formation of B2 TiNi calculated here agrees well with that in Ref.[6]. It can be seen that with the increase of Hf content, the heats of formation decrease. Thus, the corresponding phase stability of B2 $Ti_{1-x}NiHf_x$ decrease.

It has to be noted that MTT of TiNiHf alloys is related to the stability of B2 phase and B19′ phase as well. Thus, we also calculate the electronic structure of B19′ $Ti_{1-x}NiHf_x$ ($x = 0, 0.5$). Figure 5 shows their total DOS. The total DOS of B19′ TiNi is similar to that in Ref.[18]. Comparing the total DOS of B19′ $Ti_{0.5}NiHf_{0.5}$ with that of B19′ TiNi, we can find that the Fermi level is practically equal and the shape of the peak near the Fermi level is quite similar for both. So it can be considered that the electronic structure of B19′ $Ti_{1-x}NiHf_x$ remains nearly unchanged with the increase of Hf content and Hf content has little effect on the stability of B19′ $Ti_{1-x}NiHf_x$.

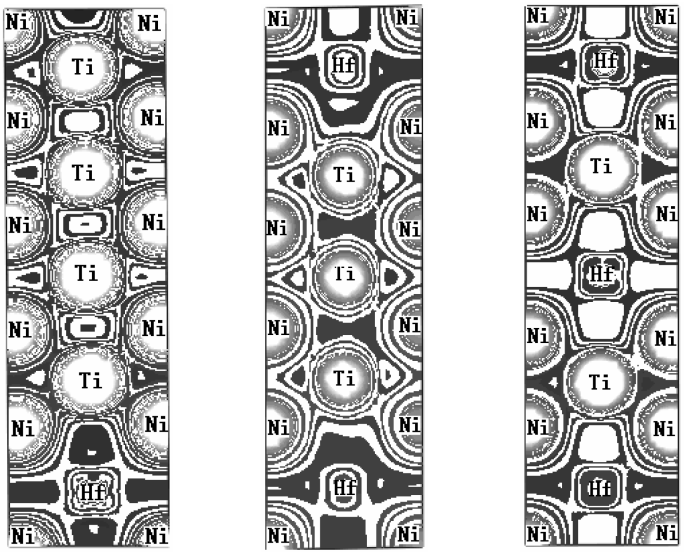


Fig.4. Charge density map in the (110) plane of B2 $Ti_{1-x}NiHf_x$: (a) for $x = 0.2$, (b) for $x = 0.4$, (c) for $x = 0.6$. The white colour and black colour denote the high and low charge density respectively.

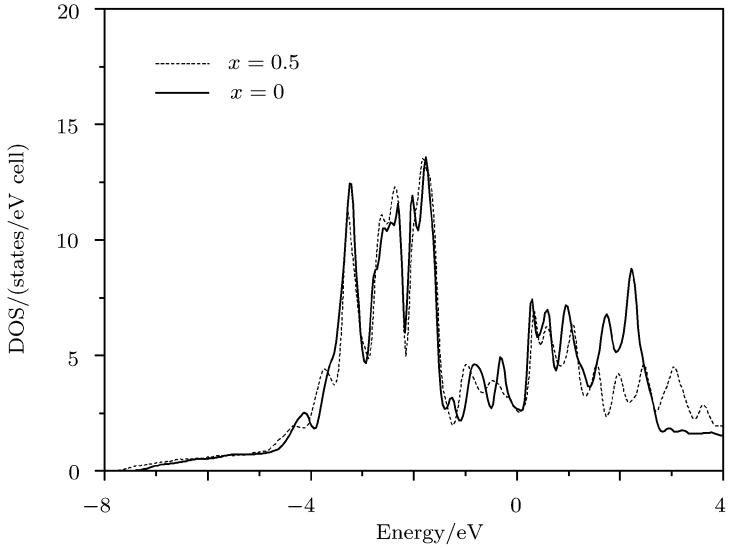


Fig.5. Total DOS of B19′ $Ti_{1-x}NiHf_x$ $(x = 0, 0.5)$.

In binary intermetallic compounds, high DOS at the Fermi level has been related to the structure instability. However, Ravi *et al* [19] argued that this may not be the case for ternary system. As is clear from our calculations, with the increase of Hf content, the DOS at Fermi level slightly lowers, but the stability of B2 $Ti_{1-x}NiHf_x$ decreases. From above discussion, it is shown that the hybridization between Ti d and Ni d states and that between Hf d and Ni d states are mainly responsible for the structure stability of B2 $Ti_{1-x}NiHf_x$. Furthermore, the hybridization between Hf d and Ni d states is weaker than that between Ti d and Ni d states, and the bandwidth of Ni d states decrease with the increase of Hf content. Thus the structure stability of B2 $Ti_{1-x}NiHf_x$ decreases with the increase of Hf content. In addition, the electronic structure and stability of B19′ $Ti_{1-x}NiHf_x$ change insignificantly with Hf content. Consequently, it can

be concluded that the increase of MTT stems from the decrease of stability of B2 $Ti_{1-x}NiHf_x$ with the increase of Hf content. We think these results will give a direction to the work of designing new high-temperature SMAs.

4. Conclusion

The electronic structure and stability of B2 $Ti_{1-x}NiHf_x$ and B19′ $Ti_{1-x}NiHf_x$ have been investigated from the first-principles. An analysis of the DOS and the charge density shows that the hybridization between Ti (Hf) d and Ni d states is mainly responsible for the stability of B2 $Ti_{1-x}NiHf_x$.The hybridization between Ti d and Ni d states is stronger than that between Hf d and Ni d states. The bandwidth of Ni d states decreases with the increase of Hf content. Thus the stability of B2 $Ti_{1-x}NiHf_x$ decreases with the increase of Hf content, which is consistent with the analysis of heats of formation. In addition, the electronic structure and stability of B19′ $Ti_{1-x}NiHf_x$ change insignificantly with Hf content. The increase of MTT arises from the decrease of stability of B2 $Ti_{1-x}NiHf_x$ when the Hf content increases.

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