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Experimental and Theoretical Studies on the C15 Intermetallic Compounds MV_2 ($M=Zr, Hf$ and Ta): Elasticity and Phase Stability

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ABSTRACT

The phase stability of C15 HfV_2 was studied by specific heat measurements. The elastic constants of C15 HfV_2 were measured by the resonant ultrasound spectroscopy. Total energy and electronic structure of C15 intermetallic compounds MV_2 ($M=Zr, Hf$ and Ta) were calculated using the linear muffin tin orbital (LMTO) method. The band structures at X-point near the Fermi level were used to understand the anomalous shear moduli of the C15 HfV_2 and ZrV_2 . It was found that the double degeneracy with a linear dispersion relation of electronic levels at the X-point near the Fermi surface is mainly responsible for the C15 anomalous elasticity at high temperatures. The densities of states at Fermi level and the geometry of the Fermi surface were used to explain the low temperature phase instability of C15 HfV_2 and ZrV_2 and the stability of C15 TaV_2 . The relationship between the anomalous elasticity and structural instability of C15 HfV_2 and ZrV_2 were also studied.

INTRODUCTION

Most intermetallics have complex structures and Laves phases constitute the single largest group. Early transition-metal Laves phase compounds have high melting temperatures, high strength, excellent oxidation resistance, e.g. C15 MV_2 ($M=Zr, Hf$ and Ta), and therefore, they are attractive candidates for high temperature structural materials studies. For these Laves phases, the crystallography, physical properties, and mechanical behavior have been subjected to experimental studies (1-4). The future goal is to understand these experimental results in order to improve its low temperature ductility and fracture toughness. The achievement of this goal depends strongly on a thorough understanding of the electronic and mechanical properties of the materials by a combination investigation of the first-principle calculations and the comprehensive experimental work (5). We report here the first-principle calculations of total energy and electronic structure and the experimental studies of elastic properties and structural stability for C15 MV_2 ($M=Zr, Hf$ and Ta).

EXPERIMENTAL PROCEDURES AND CALCULATION METHOD

In the experiments, the structural stability of C15 HfV_2+Nb was determined using sensitive specific heat measurements between 15 K and 250 K, in steps of 0.3 K, in both heating and cooling experiments. The elastic constants of C15 HfV_2+Nb were measured using the

resonant ultrasound spectroscopy. The measurements were carried out from room temperature to 70K.

In the first-principle calculations, the total energy and the electronic structure of the C15 phases were determined self-consistently using the linear muffin-tin orbital (LMTO) method with the atomic sphere approximation (ASA). The basis set included s, p and d orbitals ($l_{\max}=2$) for each site. The self-consistent iterations used 14 points in reciprocal k space along Γ -X direction in the irreducible Brillouin zone (IBZ). The total energy and the electronic band structure were determined at 372 independent k points within the IBZ. The valence states were treated in a semi-relativistic scheme (6), and the spin-orbit coupling term was neglected for the early transition metal elements. The core states were treated fully relativistically. The exchange and correlation potential used in the calculations was the von Barth-Hedin local density formalism (7).

RESULTS AND DISCUSSION

The specific heat measurement of binary C15 HfV_2 reveals that there is a very large and narrow peak at 115.5 K, indicating that a structural transformation occurs at this low temperature. This is consistent with previous work (8). The results of the specific heat measurements on a series ternary C15 compounds ($\text{V}/\text{Hf}=2$, $\text{Nb}=0.5, 1.0, 2.0, 5.0, 10.0$, and 15.0 at.%) is shown in Fig. 1.

Fig. 1 C_p vs. T of C15 HfV_2+Nb .

It can be seen from Fig. 1 that Nb addition can reduce the transition temperature and the heat absorption in the structural transformation and even a small amount of Nb addition (2-3 at.%) can eliminate this structural transformation completely. This reveals that Nb alloying stabilize the C15 structure of HfV_2 .

The elastic constants and their temperature dependence of binary C15 HfV_2 and ZrV_2 have been studied before. The results, as shown in Fig. 2, show that the shear moduli of C15 HfV_2 and ZrV_2 are anomalous in almost entire temperature region, i.e. they increase with increasing temperature (9-10). It was proposed that there a double degeneracy with a linear dispersion relation of electronic levels at the X-point of the irreducible Brillouin zone (IBZ) and the Fermi surface passes through

Fig. 2 Shear modulus vs. T of HfV_2 and ZrV_2 .

the X-point. Therefore, the electronic contribution is anomalous in entire temperature region (11). The low temperature structural transformation is induced by shear modulus softening due to the cancellation of the anomalous and negative electronic contribution to the normal and position ion contribution (11).

The shear modulus (G), Young's modulus (E), Bulk modulus (B) and Poisson's ratio (ν) of the ternary C15 $\text{Hf}_{25}\text{V}_{60}\text{Nb}_{15}$ are shown as a function of temperature in Fig. 3. It can be seen from Fig. 6 that the shear and Young's moduli increase with increasing temperature, the bulk modulus is virtually constant, and the Poisson's ratio is much higher than observed for most materials and decreases with increasing temperature. These results reveal that an anomaly in elastic properties still exists in ternary C15 compounds, although there is no low temperature structural instability in the ternary compounds. This suggests that the shear modulus anomaly is not directly related to such a phase transformation.

Fig. 3 Elastic moduli of $\text{Hf}_{25}\text{V}_{60}\text{Nb}_{15}$: (a) G vs. T , (b) E vs. T , (c) B vs. T , and (d) ν vs. T .

In order to understand these experimental results, especially the dramatic change in phase stability due to a small amount of alloying, first-principle calculations were performed, concentrating on the electronic structures of the systems. It is believed that the electronic effects are responsible for these phenomena. Total energy vs. volume curves for C15 HfV_2 and ZrV_2 are shown in Fig. 4. A similar curve can be obtained for TaV_2 . It can be obtained from these E vs. V curves that the theoretical equilibrium lattice constants are $7.5467\text{\AA}$ for ZrV_2 , $7.4740\text{\AA}$ for HfV_2 , and $7.2977\text{\AA}$ for TaV_2 , which are just 1-2% off the experimental values. The electronic structures at the equilibrium lattice constants were obtained. Fig. 5 shows the detailed feature of the band structures of C15 MV_2 ($M=\text{Zr, Hf and Ta}$) at the X-point near the Fermi level.

Fig. 4 E-V curves for C15 HfV₂ and ZrV₂.

Fig. 5 Band structure at X-point near the Fermi level.

It can be found from Fig. 5 that there is indeed a double degeneration of electron levels with a linear dispersion law in the neighborhood of the X-point of IBZ. However, the Fermi surface passes *near* the X-point with an energy gap $\Delta\epsilon$ ($\Delta\epsilon=781\text{K}$ for ZrV₂, $\Delta\epsilon=750\text{K}$ for HfV₂ and $\Delta\epsilon=1000\text{K}$ for TaV₂), instead of passing directly *through* the X-point. In this case, it can be shown that the electronic contribution to the shear modulus, c_{44}^e , is anomalous in some temperature region instead of entire temperature region (12), depending on the value of $\Delta\epsilon$, as shown in Fig. 6.

Fig. 6 c_{44}^e vs. T.

These results suggest that for C15 MV₂ (M=Zr, Hf and Ta), the electronic contribution to the shear modulus, c_{44}^e , is *negative* and anomalous at high temperatures, i.e. c_{44}^e increases with increasing temperature at high temperatures. This can explain the experimentally observed anomalous behavior of shear modulus for C15 HfV₂ at high temperatures. It is also suggested based on these arguments that the V-shaped low temperature behavior of c_{44} for C15 HfV₂ is not due to the electronic effect mentioned above because c_{44}^e shows no stiffening in the low temperature region and, therefore, the low temperature phase transformation is not caused by the cancellation of the negative electronic contribution to the shear modulus, c_{44}^e , with the corresponding positive modulus due to ion-ion interaction, c_{44}^i .

The density of states (DOS) of C15 MV_2 ($M=Zr, V$, and Ta) is shown in Fig. 7. It can be seen that for these systems, the density of states at the Fermi level, $N(E_f)$, is very large. This results in a very strong electron-phonon coupling due to the contribution of a large number of electrons. The Fermi surfaces of C15 MV_2 ($M=Zr, V$, and Ta) is shown in Fig. 8. It can be seen that C15 HfV_2 and ZrV_2 have Fermi surface nesting with a $q//<100>$ and C15 TaV_2 does not.

Fig. 7 DOS of the C15 compounds.

The Fermi surface nesting result in a very large electronic susceptibility, which induces an electronic charge density wave (along $<100>$ with a wavelength $\lambda \sim 1/q$). This electronic charge density wave may induce a structural modulation through the strong electron-phonon interaction at a low temperature. We believe that this may be the mechanism for the structural transformation in C15 HfV_2 , as described above, and C15 ZrV_2 (13). In addition, C15 TaV_2 has no such a transformation (14) due to the lack of Fermi surface nesting, as shown in Fig. 8. Based on this argument, the stabilization of C15 structure in HfV_2+Nb by Nb alloying can be understood in this way: the substitution of Hf site by Nb increases the Fermi level, resulting in the disappearance of Fermi surface nesting and a smaller $N(E_f)$.

Fig. 8 The Fermi surfaces of (a) HfV_2 and ZrV_2 , and (b) TaV_2 .

CONCLUSIONS

1. The phase stability of the C15 Laves compounds HfV_2+Nb has been investigated. The binary C15 Laves phase HfV_2 is unstable at low temperatures. A structural phase transformation occurs at about 115K. Nb ternary alloying can reduce the transition temperature and heat

absorption in the structural transformation of the C15 Laves phase HfV_2+Nb . A small amount of Nb doping (Nb at.%>2-3) can eliminate this phase transformation. This means that the role played by the Nb ternary alloying is to stabilize the structure of C15.

2. Anomalous elastic properties exist in both binary and ternary C15 Laves compounds of HfV_2+Nb . For ternary C15 compounds, the shear and Young's moduli increase with increasing temperature, the bulk modulus is virtually constant, and the Poisson's ratio is very high and decreases with increasing temperature. The special electronic structure may be one of the reasons for the C15 anomalous shear modulus at high temperatures.

3. The low temperature structural instability of C15 HfV_2 and ZrV_2 may not be directly related to its anomalous elastic properties. Low temperature structural instability of C15 HfV_2 and ZrV_2 may be induced by phonon softening, resulting from a large $N(E_f)$ and Fermi surface nesting. The lack of structure instability of C15 TaV_2 and HfV_2+Nb is due to the disappearance of Fermi surface nesting and a smaller $N(E_f)$.

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