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C15 Intermetallic Compounds HfV_2+Nb

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ABSTRACT

The phase fields and equilibria in the Hf-V-Nb system were determined using a combination of SEM, EDS and x-ray diffraction. The structural stability of the C15 HfV_2+Nb was studied by x-ray diffraction and specific heat measurements. The elastic constants of C15 HfV_2+Nb were measured by the resonant ultrasound spectroscopy technique. First-principle quantum mechanical calculations based on the local-density-functional theory have been employed to study the total energy and electronic structure of C15 HfV_2, which can be used to understand the physical and metallurgical properties of the C15 intermetallics HfV_2+Nb.

INTRODUCTION

Intermetallic compounds are attractive candidates for high temperature structural materials because of their desirable intrinsic properties [1]. There have been many investigations carried out on various compounds, but mostly on structures that are ordered forms of fcc, bcc and hcp metals. If new intermetallics are to be selected on the basis of low density and high melting temperature, then the attraction of two groups of materials becomes apparent: topologically close-packed compounds [2] and silicide-based compounds [3].

Since the discovery of superconductivity in Laves phases, much attention has been paid to the study of plastic deformation in these alloys and to the Hf-V-Nb system in particular [4]. It was found that mechanical twinning is the main deformation mode in C15 Hf-V-Nb alloys during compression tests at room temperature [5-6]. This suggests that mechanical twinning is potentially very important in the deformation of topologically close-packed intermetallic compounds in general. Recently, more studies have been made for complex intermetallic compounds, especially C15 Laves compounds [6-9]. This paper describes our work on phase equilibria, phase stability, and elastic properties of C15 intermetallic compounds HfV_2+Nb, as part of a broader study of topologically close-packed intermetallics.

EXPERIMENTAL PROCEDURES AND CALCULATION METHOD

For locating the Laves phase fields and determining the phase diagram of the Hf-V-Nb system, arc-melted buttons were studied using optical microscopy, powder x-ray diffraction (XRD) and energy dispersive spectroscopy (EDS) techniques. The overall composition of each sample and compositions of each phase were measured using EDS. Three or four individual analyses were performed for each phase. Results on samples showing standard deviations greater than 2 at.% were eliminated. Powder x-ray diffraction experiments were conducted on samples of the single phase compositions to check their crystal structures.

For examining the C15 phase stability, a single phase C15 alloy of composition $Hf_{30}V_{55}Nb_{15}$ was chosen based on the phase diagram for high temperature study. High temperature XRD was performed at temperatures ranged from room temperature to 700°C. The low temperature phase stability of the ternary C15 Laves compound was examined by heat capacity measurements. The specific heat, C_p, was measured from 15K to 250K to investigate any phase transformation, in steps of 0.3K.

We also measured the elastic constants of the polycrystalline C15 $Hf_{25}V_{60}Nb_{15}$ using the resonant ultrasound spectroscopy technique (RUS) [10]. To study the temperature dependence of the elastic properties of the ternary C15 compound, the measurements were carried out from

room temperature to 70K, using boil-off gas of a liquid helium storage dewar and a temperature controller.

In the first-principle calculations, the total energy and the electronic structure of C15 HfV_2 were determined self-consistently using the linear muffin-tin orbital (LMTO) method with the atomic sphere approximation (ASA). The ideal radius ratio for C15 HfV_2, r_{Hf}/r_V=1.225, was used. 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 details of the calculation were presented in Ref. [11].

RESULTS AND DISCUSSION

Phase Diagram of the Hf-V-Nb System

Figure 1 shows an isothermal section of the Hf-V-Nb phase diagram at 1000°C [12]. The regions representing the extent of the cubic C15 Laves phase based on HfV_2 (λ_2), the hexagonal C14 Laves phase (λ_1) and ternary b.c.c. phases (δ) are noted. The x-ray diffraction patterns of the C15 and C14 Laves phases are shown in Fig. 2.

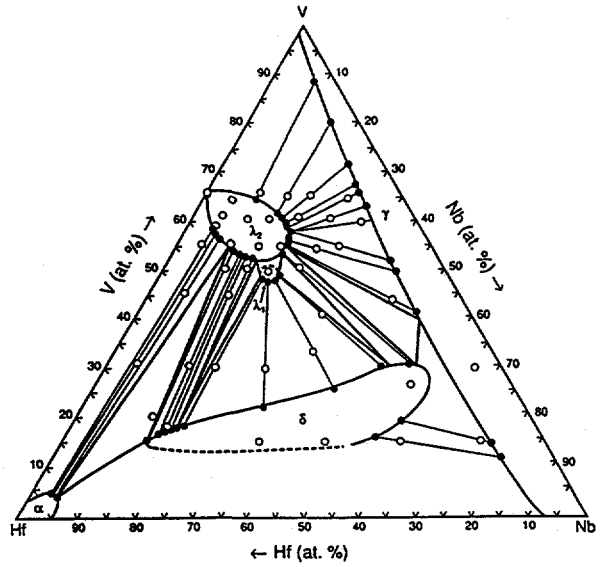

Fig. 1 The Hf-V-Nb equilibrium phase diagram at 1000°C. o : composition tested; • : composition of each phase; —— : tie-lines; ▬▬ : established phase boundaries; ▪▪▪▪ : approximate phase boundaries. λ_2 = C15; λ_1 = C14 ; γ = b.c.c. solid solution; δ = b.c.c. solid solution (Ref. [12]).

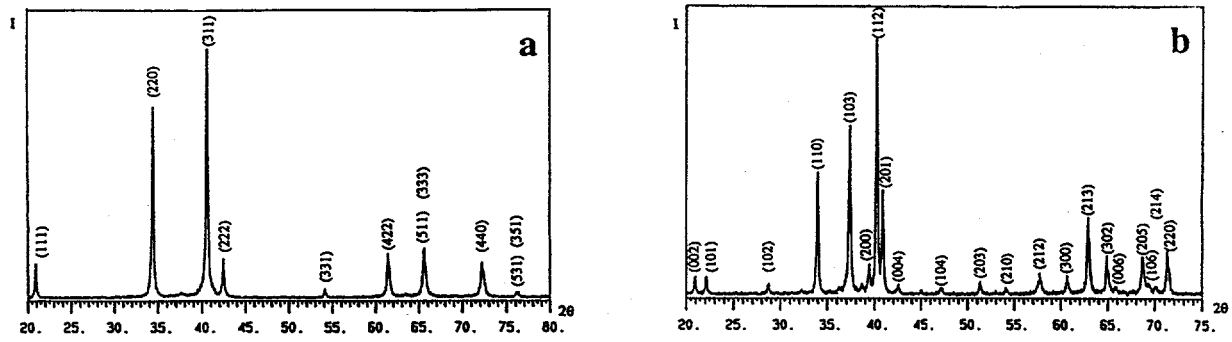

Fig. 2 (a) XRD pattern of the C15 phase, and (b) XRD pattern of the C14 phase (Ref. [12]).

C15 Phase Stability

Using the phase diagram of the Hf-V-Nb system, the phase stability of the C15 intermetallic compound based on HfV_2 was studied.

(a) High temperature phase stability

X-ray diffraction patterns of a single phase C15 alloy, $Hf_{30}V_{55}Nb_{15}$, obtained at different temperatures unambiguously show that there is no structural transformation in this alloy between room temperature and 700°C, i.e., the ternary C15 Laves phase based on HfV_2 is thermally stable over this entire temperature range [13].

(b) Low temperature phase stability

Specific heat measurements from the five single phase samples, with the compositions of V/Hf=2 and Nb at.%=0.0, 0.5, 1.0, 2.0, and 5.0, respectively, at low temperatures are shown in Fig. 3. Figure 3 reveals that the binary C15 Laves phase HfV_2 is unstable at low temperatures. A structural phase transformation occurs at about 115K. Further transmission electron microscopy study using a liquid nitrogen stage unambiguously shows that this is a structural transformation, because of the appearance of superlattice spots in diffraction patterns. Figure 3 also shows that Nb ternary alloying can reduce the transition temperature and heat absorption in the structural transformation of the C15 Laves phase HfV_2+Nb, and in fact small Nb additions of 2-3 at. % eliminate this structural phase transformation entirely. This means that Nb ternary alloying stabilizes the structure of C15.

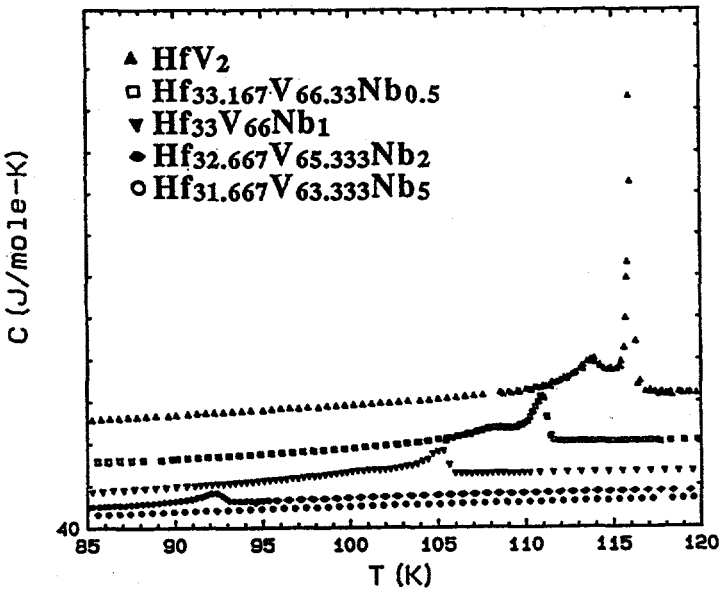

Fig. 3 Heat capacity vs. temperature curves for five ternary C15 Laves compounds based on HfV_2 in the vicinity of the lattice transformation temperature.

Elastic Properties

The elastic constants of binary C15 HfV_2 have been studied. It has been found that its elastic properties are anomalous, in that its shear modulus increases with increasing temperature [14-15]. It was suggested that the electronic contribution to the shear modulus is anomalous, based on the *assumption* that the Fermi surface passes *through* the X-point of the irreducible Brillouin zone (IBZ) and the there are double degenerate energy levels with a linear dispersion relation in the neighborhood of the X-point [16]. It was also suggested that the low temperature structural instability of C15 HfV_2 is attributed to this anomalous shear modulus [16].

The shear modulus (G), Young's modulus (Y), Bulk modulus (B) and Poisson's ratio (v) of the ternary C15 $Hf_{25}V_{60}Nb_{15}$ are shown as a function of temperature in Fig. 4. It can be

seen from Fig. 4 that the shear and Young's moduli increase with increasing temperature, the bulk modulus is virtually constant, and the Poisson's ratio (ν=0.4) is higher than observed for most materials (ν=0.3) 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 the structural instability.

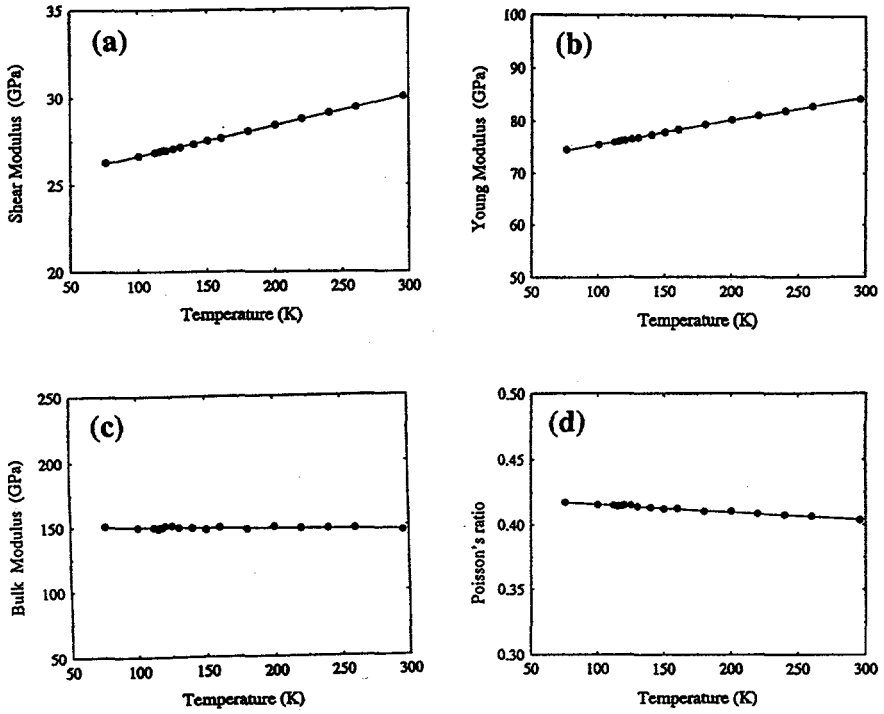

Fig. 4 Temperature dependence of elastic constants of C15 $Hf_{25}V_{60}Nb_{15}$: (a) G vs. T, (b) Y vs. T, (c) B vs. T, and (d) ν vs. T (Ref. [10]).

Theoretical Approach

Total energy and electronic structure calculations of C15 HfV_2 by LMTO-ASA shows that the density of states (DOS) at the Fermi level, $N(E_F)$, is very large, as shown in Fig. 5, and there is Fermi surface nesting with a nesting vector **q**//<100> in IBZ, as shown in Fig. 6.

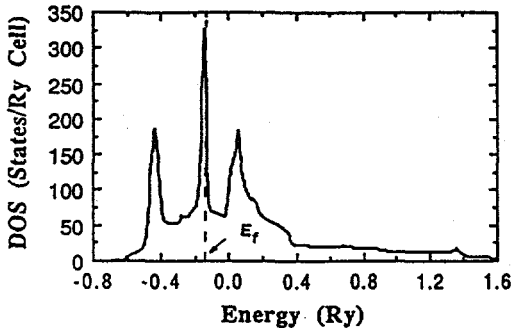

Fig. 5 DOS of C15 HfV_2, showing a large $N(E_F)$.

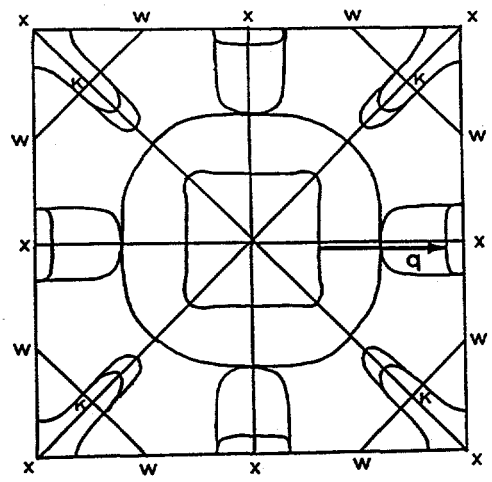

Fig. 6 <001> section of the Fermi surface, showing Fermi surface nesting (**q**//<100>).

The Fermi surface nesting results 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 a strong electron-phonon interaction, because of a very large $N(E_F)$, at low temperatures. We believe that this could be the mechanism for the structural transformation in the binary C15 HfV_2. The Fermi level is increased due to Nb alloying in the C15 HfV_2, resulting in a smaller $N(E_F)$ and the absence of Fermi surface nesting. Therefore, C15 HfV_2+Nb is structurally stable at low temperatures.

The calculation also shows that there is indeed a double degeneration of electron levels with a linear dispersion relation in the neighborhood of the X-point of IBZ [11]. However, the Fermi surface passes *near* the X-point with an energy gap $\Delta\varepsilon$(=750K), instead of passing directly *through* the X-point, as shown in Fig. 7. In this case, it can be shown that the electronic contribution to the shear modulus, c_{44}^e, is anomalous, depending on the value of $\Delta\varepsilon$ [11], as shown in Fig. 8.

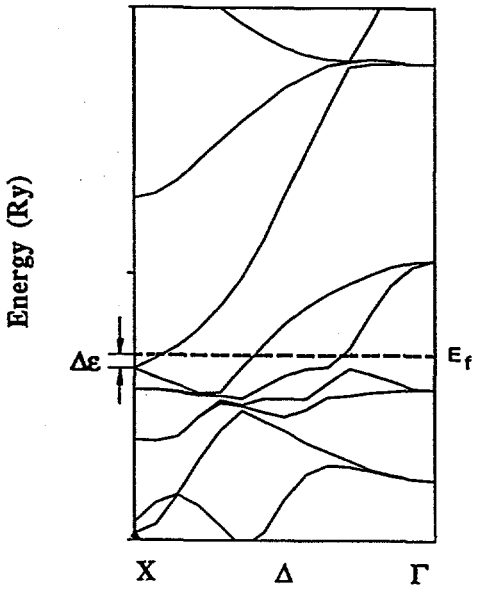

Fig. 7 Detailed features of the band structure near the Fermi level for C15 HfV_2, showing the double degeneration with a linear dispersion relation and energy gap.

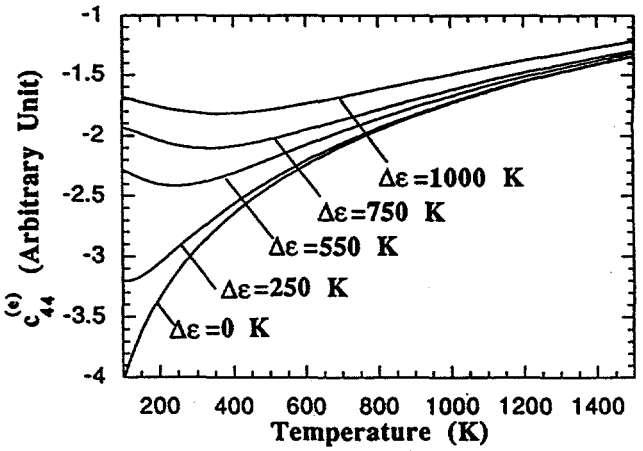

Fig. 8 Calculated temperature dependence of c_{44}^e for different $\Delta\varepsilon$.

These results suggest that for C15 HfV_2 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 HfV_2 at high temperatures [15].

CONCLUSIONS

1. The equilibrium phase field of the cubic Laves phase based on HfV_2 at 1000°C in the Hf-V-Nb system has been located. This phase field is relatively large, with a compositional range of 0 to 20 at. % Nb. A previously-unknown ternary C14 hexagonal Laves phase field has been found, which is small relative to the C15 phase field.

2. The phase stability of the C15 Laves compounds HfV_2+Nb has been investigated.

(a). There is no structural transformation in this alloy between room temperature and 700°C, i.e., the ternary C15 Laves phase based on HfV_2 is thermally stable at high temperatures.

(b). 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. The low temperature structural instability of C15 HfV_2 may be induced by phonon softening, resulting from a very large $N(E_F)$ and Fermi surface nesting.

3. 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 near the Fermi level at the X-point of IBZ may account for the anomalous shear modulus at high temperatures.

4. The low temperature structural instability of C15 HfV_2 may not be directly related to its anomalous shear modulus.

ACKNOWLEDGMENTS

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REFERENCES

1. D. P. Pope and C. T. Liu, in *Superalloys, Supercomposites and Superceramics*, ed. by J. K. Tien, and T. Caulfield, 583-624 (Academic Press, New York) (1989).
2. D. P. Pope and F. Chu, in *Structural Intermetallics*, ed. by Darolia, Lewandowski, Liu, Martin, Miracle, and Nathal, 637-646 (TMS Publication, Warrendale, PA) (1993).
3. T. E. Mitchell, R. G. Castro, J. J. Petrovic, S. A. Maloy, O. Unal, and M. M. Chadwick, Mater. Sci. & Eng., **A155**, 241-250 (1992).
4. K. Inoue and K. Tachikawa, IEEE Trans. Mag., **Mag-13**(1), 840-843 (1977).
5. J. D. Livingston and E. L. Hall, J. Mater. Res. **5**(1), 5-8 (1990).
6. F. Chu and D. P. Pope, Mater. Sci. & Eng., **A170**, 39-47 (1993).
7. M. Takeyama, and C. T. Liu, Mater. Sci. & Eng., 61-66 **A132** (1991).
8. P. M. Hazzledine, in *Twinning in Advanced Materials*, ed. by Yoo and Wuttig, 403-414 (TMS Publication, Warrendale, PA), (1994).
9. D. J. Thoma and J. H. Perepezko, Mater. Sci. & Eng., 97-108 **A156**, (1992).
10. F. Chu, Ming Lei, A. Migliori, S. P. Chen and T. E. Mitchell, Phil. Mag. B, **70**, 867 (1994).
11. F. Chu, M. Sob, R. Siegl, T. E. Mitchell and S. P. Chen, Phil. Mag. B, **70**, 881 (1994).
12. F. Chu and D. P. Pope, Scripta Met. et Mat. **26**, 399 (1992).
13. F. Chu and D. P. Pope, Scripta Met. et Mat., **28**, 331, (1993).
14. T. R. Finlayson, E. J. Lanston, M. A. Simpson, E. E. Gibbs, and T. F. Smith, J. Phys. F., **8**(1), 2269-2278 (1978).
15. A. S. Balankin and D. M. Skorov, Sov. Phys. Solid State, **24**(4), 681-682 (1982).
16. Y.A. Izyumov, V. Y. Naysh, and V. N. Syromyatnikov, Fiz. Metal. Metalloved., **39**(3), 455-460 (1975).