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LAVES PHASE TERNARY SYSTEM

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FIRST-PRINCIPLES TOTAL ENERGY STUDY OF NbCr₂ + V LAVES PHASE TERNARY SYSTEM

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ABSTRACT

The C15 NbCr₂ + V Laves phase ternary system is studied by using a first-principles, self-consistent, full-potential total energy method. Equilibrium lattice parameters, cohesive energies, density of states and formation energies of substitutional defects are calculated. Results of all these calculations show that in the C15 NbCr₂ + V compounds, V atoms substitute Cr atoms only.

INTRODUCTION

Among the intermetallic compounds studied for use as high-temperature structural materials, Laves phases have been attracting an increasing attention. Laves phase compounds are intermetallic compounds of composition AB₂ and they have highly symmetric crystal structures: cubic C15 (MgCu₂), hexagonal C14 (MgZn₂) and dihexagonal C36 (MgNi₂)[1]. These crystal structures are topologically closed-packed (TCP) structures; assuming hard spheres, atomic volume accounts for about 71% of the unit cell volume.

A number of Laves phase compounds have properties that are quite desirable for high-temperature structural applications, such as high melting temperatures, low densities and high oxidation resistance[2]. The C15 Laves phases have so far been studied more exclusively compared to the other two, primarily because of the availability of more slip systems in the fcc-lattice-based C15 structure. A C15 compound of particular interest is NbCr₂. This compound has been subject to quite extensive experimental [3-7] and theoretical [8-12] studies. NbCr₂ has a high melting temperature (1730 °C), reasonable oxidation resistance, high strength, excellent creep behaviour and intermediate density (7.7 g/cm³)[13,14]. However, as is also true for the other TCP compounds in general, poor low-temperature ductility is a major obstacle in the use of C15 NbCr₂ in practical applications. Consequently, in recent years there have been focused efforts in finding ways to improve its low-temperature ductility without compromising much on its attractive high-temperature properties [13-17]. The central idea behind these studies is adding a third metal to form a ternary alloy. The particular C15 NbCr₂-based systems that are studied are NbCr₂ + V [13-16], NbCr₂ + Ti [18], NbCr₂ + Be and NbCr₂ + Mo [19]. Another example of this approach in the context of C15 Laves phases is the HfV₂ + Nb system [15,20-23].

In this study we will confine our interest to the NbCr₂ + V system for which there exists quite an extensive body of experimental results [13-16]. By using a full-potential linear muffin-tin orbital (FP-LMTO) method based on the local density approximation (LDA) to the density functional theory [24], we carried out total energy calculations to understand the electronic structures of the C15 Laves phase NbCr₂ + V compounds. These calculations will enable us to account for the major experimental findings; namely, (i) the lattice parameter increases linearly with the vanadium content, (ii) the C15 phase region in the ternary phase diagram of the Nb-Cr-V extends towards vanadium by up to more than 30 at.% of V, (iii) V atoms replace Cr atoms only.

We proceed by describing the calculational method. We, then, present the computational results and compare them with their experimental counterparts. We continue by discussing the implications of our results, and conclude by a summary.

CALCULATIONAL METHOD

We performed self-consistent *ab initio* total energy calculations to study various properties of the NbCr₂-based Laves phase compounds obtained by vanadium addition. The computed quantities fall into two categories. The equilibrium lattice constants, cohesive energies, and density of states at the Fermi level, $N(E_F)$, all as functions of atomic V concentration are in one category. In the other category, we have the formation energies of the substitutional defects. We carried out two sets of calculations corresponding to these two categories of physical quantities.

These calculations were carried out with a full-potential, all-electron electronic structure method that uses a linear-muffin-tin-orbital basis set [25]. Basis functions, electron densities and potentials were expanded in spherical harmonics through $l=6$ within non-overlapping muffin-tin spheres, and in Fourier series in the interstitial region. We used the Hedin-Lundquist [26] form of the LDA exchange-correlation functional with random phase approximation parameters [27]. Brillouin zone integrations were performed with Fourier quadrature [28] with Gaussian smearing. For the calculation of the quantities falling into the first category, we used the 6-atom primitive cell of the C15 structure. The formation energies of the substitutional defects were calculated using the conventional 24-atom cell. The details for each type of calculations are as follows.

For a C15 compound of AB₂, there are 2 sites for the element A, and 4 symmetrically equivalent sites for the element B in the 6-atom cell. Since all the experimental evidence points to V atoms occupying Cr, *i.e.* B, sites [13-16], we considered the compounds Nb₃₃Cr₅₀V₁₇ and Nb₃₃Cr₃₃V₃₃, which are in the C15 region of the Nb-Cr-V phase diagram [13,16]. The former compound corresponds to a unit cell obtained by replacing one chromium atom in the 6-atom cell by one vanadium atom (single-substitution case). The latter, on the other hand, corresponds to two vanadium atoms replacing two chromium atoms in the 6-atom cell (double-substitution). The results of experimental investigations by Chu *et al.* [13-16] imply a random distribution of V atoms on the symmetrically equivalent Cr sites. Therefore, these calculations based on the 6-atom unit cell should be sufficient.

The number of inequivalent special **k**-points in the irreducible Brillouin zone was 58 and 78 for the single- and double-substitution calculations, respectively. Convergence was tested up to 91 and 126 points, respectively and total energies changed by less than 0.2 mRy/cell. Both calculations were fully relativistic. The basis set used $2x(3s,3p) + 3x(4s,4p) + 2x(3d)$ orbitals on each V and Cr site. This notation means that, for example, chromium 3s orbitals with two different interstitial kinetic energies were included in the basis set. Each Nb site contributed $2x(4s,4p) + 3x(5s,5p) + 2x(4d)$ orbitals.

We carried out two calculations in the 24-atom cell to compute formation energies of two possible substitutional defects: (i) one V atom replacing a Nb atom, (ii) one V atom replacing a Cr atom. The former compound will be denoted by Nb₇VCr₁₆, and the latter by Nb₈VCr₁₅. The number of inequivalent special **k**-points in the irreducible Brillouin zone was 10 and 28 for the Nb₇VCr₁₆ and the Nb₈VCr₁₅ calculations, respectively. Both sets correspond to 216 points in the full zone. These calculations were scalar-relativistic. The basis set consisted of two basis functions for each orbital. The semi-core *s* and *p* orbitals were included in the basis set in addition to the valence *s*, *p* and *d* orbitals.

In all calculations: (i) a total of four interstitial kinetic energies were used, (ii) all basis functions were contained in a single, fully hybridised Hamiltonian matrix.

The results for the binary NbCr₂ (0 at.% of V case), were taken from our earlier work[11].

RESULTS AND DISCUSSION

Calculated Values and Comparison with Experiment

In a series of papers Chu *et al.* [13-16] presented their experimental results on various C15 NbCr₂ + V compounds. Some of these results that are of interest in this paper can be summarised as follows. The lattice parameter depends on the atomic V concentration linearly. The C15 phase region in the Nb-Cr-V phase diagram is parallel to the Cr-V baseline, suggesting that V atoms occupy Cr sites. The linear variation of the lattice parameter as a function of the atomic V content also supports this suggestion, and in addition, it implies a random occupation of Cr sites. The alloying of NbCr₂ with V substantially extends the C15 region; ternaries containing up to more than 30 at.% of V are expected to have the C15 structure [13,16]. Now, with these in mind, we turn to the presentation and discussion of computational results.

We obtained total energy - volume curves for Nb₃₃Cr₅₀V₁₇ and Nb₃₃Cr₃₃V₃₃ by fitting the calculated values to the Birch-Murnaghan equation of state [29]. The minimum of these curves gives the theoretical equilibrium volumes, which are usually up to about 10% smaller than experimental equilibrium volumes, owing to the overbinding nature of LDA. We extracted the lattice parameters from the theoretical equilibrium volumes. The theoretical lattice parameters turned out to be about 2.3% smaller than their experimental counterparts; and they replicate the linear variation of the experimental lattice constants [13,14] as a function of atomic vanadium content (see Fig.1). Since the theoretical calculations were carried out by substituting Cr atoms with V atoms, this perfect agreement lends support to the view that V atoms replace Cr atoms only.

We computed density of states for both the single- and double-substitution cases. The total density of states curves computed for both compounds are almost identical, especially in the vicinity of Fermi levels (see Fig.2). These curves are also very similar to that of the C15 NbCr₂ [11, see Fig.4]. This result suggests that a rigid-band approach may be used in the discussion of the electronic properties of these materials. Hence, we can analyse the variation of the Fermi level, E_F , as a function of V content by assuming a fixed density-of-states vs energy curve, and then considering the effect of V addition on the number of valence electrons in the resulting ternary compound.

In all the three cases the Fermi levels are on the anti-bonding side of a valley. For NbCr₂, the Fermi level cuts the density of states curve at a relatively high value of 115.8 States/Ry. At 16.7 at.% of V concentration, $E_F = 10.47$ eV, $N(E_F) = 62.0$ States/Ry. and at 33 at.%, $E_F = 10.25$ eV, $N(E_F) = 46.9$ States/Ry. Therefore, the trend suggested by these results is that as V content is increased E_F decreases and the Fermi level intersects the density-of-states curve at lower values. Since, the density of states at the Fermi level for the binary compound is high, upon addition of a third metal, the system would like to lower $N(E_F)$ by moving the E_F position towards the minimum of the valley, which occurs at $E \sim 10.0$ eV. Now, Cr has 6 valence electrons compared to 5 for V and Nb. So, if V were to substitute for Nb, then the total number of valence electrons in the compound would not change, and that would imply that E_F position would not be affected much. Thus, V substituting Nb would not be a step towards a more stable compound. However, if V atoms replace Cr atoms, then each substitution will decrease the total number of valence electrons, thereby pulling the Fermi level down. We may anticipate that as V content is increased E_F will continue moving down until it hits the minimum of the valley at about 10.0 eV. If we consider this point as the limit for which NbCr₂ + V will crystallise in the C15 structure, then we

can easily understand why the C15 region in the ternary phase diagram extends to V concentrations in excess of 30 at.% [13,16]. Our double-substitution calculation already corresponds to 33 at.% of V, and there is still some room for E_F to drop (about .25 eV), implying the possibility of even higher V concentrations.

The cohesive energies were computed as 10.153 eV/atom (9.995 eV/atom) for the single-substitution (double-substitution) case. The cohesive energy for the base compound NbCr₂ was computed earlier [11] as 6.08 eV/atom. Thus, we see that V alloying is increasing the cohesive energy. Since, for most metals and intermetallic compounds, the larger the cohesive energy the higher the melting temperature, the C15 NbCr₂ + V ternaries are expected to have higher melting points than NbCr₂.

Formation Energies of Substitutional Defects

Although the results of the previous subsection provide very strong support to the view that V atoms substitute Cr atoms, we also computed the formation energies for a single substitutional defect in the 24-atom unit cell to gain further insight into the issue of point defects in the C15 phase. We used the expressions given below to compute the formation energies for (i) V substituting Nb, ΔE_1 , and (ii) V substituting Cr, ΔE_2 :

$$\Delta E_1 = E(\text{Nb}_7\text{VCr}_{16}) + E(\text{Nb}) - E(\text{Nb}_8\text{Cr}_{16}) - E(\text{V}) \quad (1)$$

$$\Delta E_2 = E(\text{Nb}_8\text{VCr}_{15}) + E(\text{Cr}) - E(\text{Nb}_8\text{Cr}_{16}) - E(\text{V}) \quad (2)$$

Here, the elemental energies refer to the bcc metal energies. We obtained a positive value for ΔE_1 , 0.73 eV/cell, indicating that substitution of a Nb atom by a V atom *increases* the energy. For ΔE_2 , however, we obtained -0.41 eV/cell. Therefore, when V is added to C15 NbCr₂, V atoms are expected to favour Cr sites, since this substitutional defect lowers the total energy compared to that of the original binary compound.

SUMMARY

Results of first-principles total energy calculations on the C15 NbCr₂ + V compounds have been presented. The computed equilibrium lattice parameters are in good agreement with the experimental results. The computed values of the formation energies of V replacing either a Nb or a Cr, and arguments based on the density of states clearly show that V atoms should replace Cr atoms. This finding is in perfect agreement with conclusions drawn from the experimental studies [13-16].

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Fig. 1

Fig. 3a

Fig. 3b