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Solid-solution strengthening: Substitution of V in Ni_3Al and structural stability of $Ni_3(Al,V)$

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Several questions relating to solid-solution strengthening in Ni_3Al—substitution of V and its effect on the stability of the $L1_2$ structure of Ni_3Al—are addressed using an all-electron total-energy local-density approach. By comparing the total energies of two ($L1_2$-like and $D0_{22}$-like) different structures of $Ni_3(Al_{0.5},V_{0.5})$, greater stability of the $L1_2$ structure for ternary additions of V compared with the $D0_{22}$-like structure is found (i.e., for V substitution on Al rather than Ni sites).

I. INTRODUCTION

Solid-solution strengthening is one of the technologically important features of Ni_3Al; thus, Ni_3Al can accept into solution substantial alloying additions without losing its long-range order. Clearly, knowledge of the preferential occupancy by ternary additions in Ni_3Al is fundamental for understanding strenghtening effects in Ni_3Al and for the development of superalloys for practical use.[1] The alloying behavior of Ni_3Al was first studied in detail by Guard and Westbrook;[2] their results suggested that the alloying behavior is determined by chemical effects (e.g., the electronic structure) rather than simply by size factors. Even today, there still exists a rather poor theoretical understanding of the electronic structure of Ni_3Al containing transition-metal elements in solution. Morinaga *et al.*[3] studied the alloying behavior using the discrete variational (DV) $X\alpha$ cluster method and attempted to explain the substitutional behavior by invoking the resemblance of the profile in the density of states (DOS) of the elemental additions to that of either Al or Ni. Thus they suggested that both Ti and V are elements which show a preferential occupancy at Al sites due to the similarities in the profiles of the DOS between Ti, V, and Al. In such cases, they argued, there is little effect on either the electronic structure and charge density around the substitutional site. When transition-metal additions are dissolved into Ni_3Al, it is expected that a strong hybridization between the additions and the host will occur,[4] which Morinaga *et al.*[3] did not fully take into account. In addition, different occupancies by ternary additions in compounds will yield various new phases, hence the preferential occupancy by ternary additions is closely related to the competition between different phases, i.e., phase stability.

The present work attempts to understand the effects of ternary additions of V in Ni_3Al and, in particular, the effect of V on the stability of the $L1_2$ structure of Ni_3Al. We employ the all-electron total-energy local-density formalism,[5] as carried out with the linear muffin-tin orbital (LMTO) method.[6] Comparison of total energies of two different structures ($L1_2$-like and $D0_{22}$-like) of $Ni_3(Al_{0.5},V_{0.5})$ shows that ternary additions of V in the $L1_2$-like structure are more stable than V additions in the $D0_{22}$-like structure. Furthermore, these model calculations indicate that the $L1_2$-like Ni_3Al can dissolve up to 50% V, replacing Al in an ordered way, and still retain the $L1_2$-like structure with a lower energy than in the $D0_{22}$-like structure.

II. METHOD

The total energy and the electronic structure were determined self-consistently using the linear muffin-tin orbital method within the atomic-sphere approximation.[6] The basis set included *s*, *p*, and *d* orbitals for each site. The valence states were calculated in a semirelativistic approximation and the core states were treated fully relativistically. The exchange and correlation potential of von Barth and Hedin was used.[7] Since we employed the linear tetrahedron method to calculate the density of states, the charge density, and the total energy, we investigated the relationship between the precision of the calculated physical quantities and the number of *k* points employed in the calculation. Thus we compared the total energies for different structures after extrapolating to an infinite number of *k* points so as to avoid any error caused by use of a finite number of *k* points.[8] In general, the total energy and the electronic structure were found to be well determined at 35 *k* points within the $\frac{1}{16}$ irreducible (tetragonal) Brillouin zone (IBZ). Tetragonal cells were used for both $L1_2$-like and $D0_{22}$-like structures (cf. Fig. 1); the ratio c/a was kept as a constant (at 2.036), and, for simplicity, the same radius was chosen for the Wigner-Seitz spheres for the Ni, Al, and V atoms. A parabolic fitting procedure was employed for obtaining the bulk modulus; since its calculation requires the second derivative of the total energy, the value determined involves some numerical uncertainty, with an error typically $\sim 10\%$.[8]

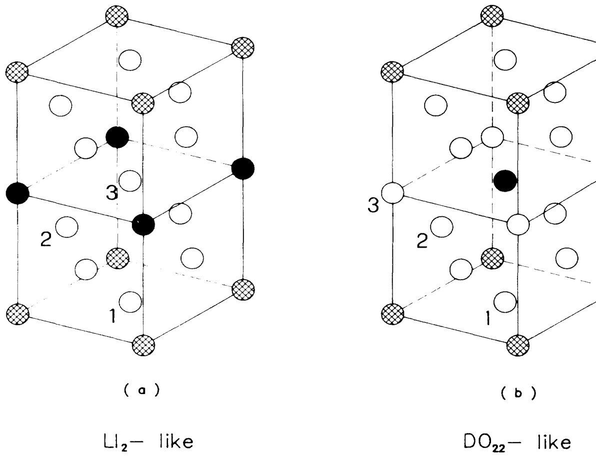

FIG. 1. The two simplest structures of $Ni_3(Al,V)$ in the (a) $L1_2$-like structure and (b) $D0_{22}$-like structure, and 1, 2, and 3 indicate the three types of Ni: Here the open circle denotes Ni, the crosshatched circle denotes Al, and the solid circle denotes V atoms.

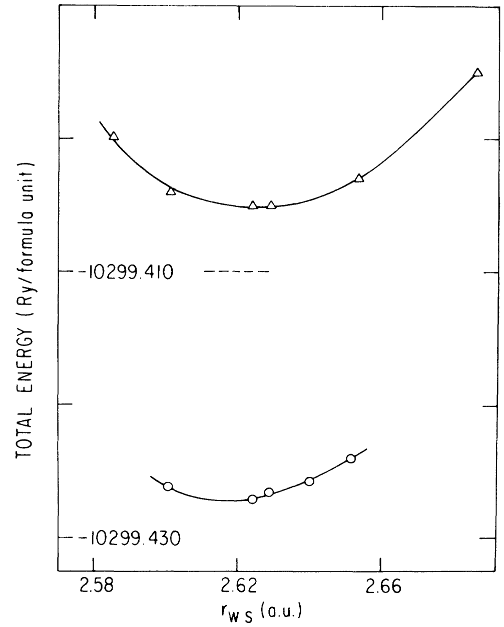

FIG. 2. Total energy as a function of the Wigner-Seitz radius for $Ni_3(Al,V)$ (△) $D0_{22}$-like and (○) $L1_2$-like structure; minimum values of total energy are −10 299.405 and −10 299.4270 Ry per formula unit for $D0_{22}$-like and $L1_2$-like structure, respectively, using 35 k points within the $\frac{1}{16}$ IBZ; the dashed line indicates the sum of the separate equilibrium values of the total energy of the Ni_3Al ($L1_2$ structure) and the Ni_3V ($D0_{22}$ structure) using 60 k points within $\frac{1}{48}$ and $\frac{1}{16}$ IBZ, respectively.

III. RESULTS AND DISCUSSION

Ni_3Al has the fcc derivative Cu_3Au or $L1_2$ structure. As shown in Fig. 1, with substitution of V atoms on Al sites in the $L1_2$ structure [Fig. 1(a)] or on Ni sites in the $D0_{22}$ structure [Fig. 1(b)] respectively, the two simplest structures of $Ni_3(Al,V)$, which are called the $L1_2$-like and $D0_{22}$-like structures, respectively, will be formed. The total energies of these two structures of $Ni_3(Al,V)$ as a function of the Wigner-Seitz radii are shown in Fig. 2. It is clearly seen that $Ni_3(Al,V)$ in the $L1_2$-like structure is energetically favored over the $D0_{22}$-like structure, because in the entire range the total energies of the $L1_2$-like structure are ~0.3–0.4 eV per formula unit lower than those of the $D0_{22}$-like structure. It is of some interest to note that in a separate study,[9] we found that the energy of Ni_3Al in the $L1_2$ structure is 0.18 eV per formula unit lower than in the $D0_{22}$ structure, and 0.16 eV per formula unit lower than in the $D0_{19}$ structure. Furthermore, it is interesting that the sum of the total energies of Ni_3Al ($L1_2$ structure) and Ni_3V ($D0_{22}$ structure) is 0.19 eV per formula unit

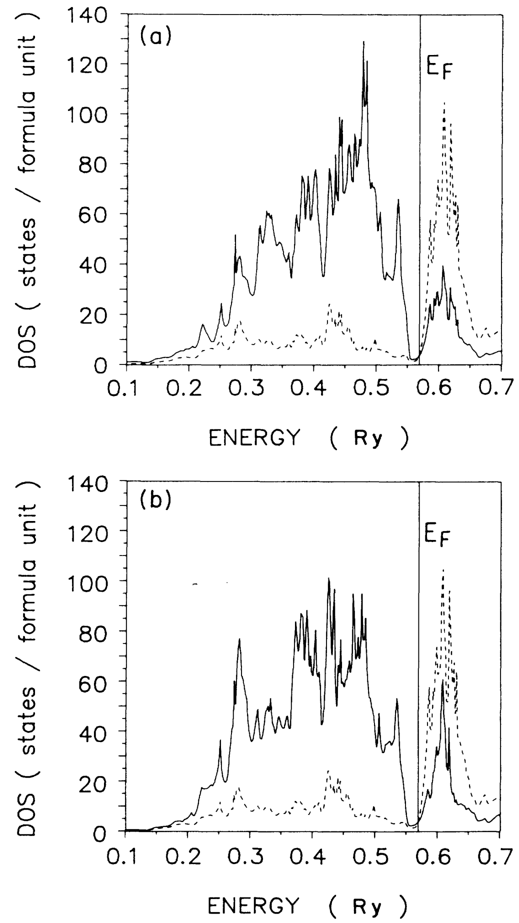

FIG. 3. Ni-d and V-d partial density of states for $Ni_3(Al,V)$ in the $L1_2$-like structure: solid line, Ni-d; dashed line, V-d: (a) Ni(2)-d and V-d [with the Ni(2) contribution scaled by a factor of 2], (b) Ni(3)-d and V-d [with the Ni(3) contribution scaled by a factor of 0.5].

higher than the total energy of $Ni_3(Al,V)$ in the $L1_2$-like structure, and 0.11 eV per formula unit lower than that in the $D0_{22}$-like structure. These results support the idea that when V atoms are dissolved as a solid solution into Ni_3Al, they preferentially occupy the Al sites, keeping the $L1_2$ structure, in agreement with observation.[2] In addition, our result for this model calculation seems to indicate that the $L1_2$-like ordered structure for Ni_3Al can be stabilized with up to 50 at. % V substitution on the Al sites.

Moreover, the phase stability of $Ni_3(Al,V)$ can be analyzed in terms of the bonding character between additions and host. This can be done despite the fact that the bonding character of Ni_3Al remains controversial. Miedema[10] emphasized that the dominant contribution to the heat of formation of Ni_3Al arises from the *p* electrons of Al by means of *p*-*d* hybridization. This conclusion was criticized by Hackenbracht and Kübler,[11] who believed that the Ni *d* – Al *d* interaction seems to be responsible for the cohesive energy of Ni_3Al. When V is dissolved into Ni_3Al, the situation becomes different from that of Ni_3Al. The heat of formation of the compound results from a competition between two dominant physical factors.[12] In our case, the weakening of the transition-metal bonds by the lattice dilatation due to accommodation of the non-transition-metal is nearly the same for both the $L1_2$-like and $D0_{22}$-like structures of $Ni_3(Al,V)$; on the other hand, we would expect that the strong *d*-*d* interaction which occurs in Ni_3Al due to V additions will be different in

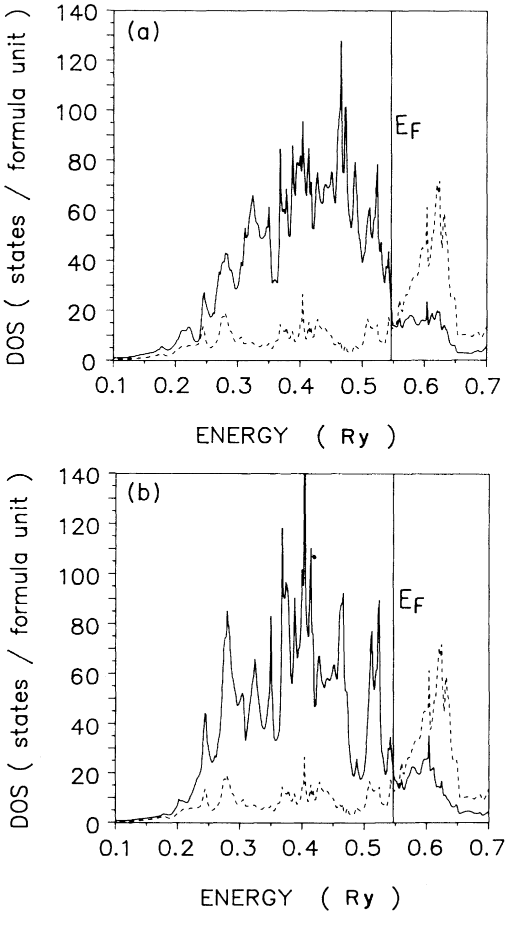

FIG. 4. Ni-*d* and V-*d* partial density of states for $Ni_3(Al,V)$ in the $D0_{22}$-like structure: solid line, Ni-*d*; dashed line, V-*d*: (a) Ni(2)-*d* and V-*d* [with the Ni(2) contribution scaled by a factor of 2], (b) Ni(3)-*d* and V-*d* [with the Ni(3) contribution scaled by a factor of 0.5].

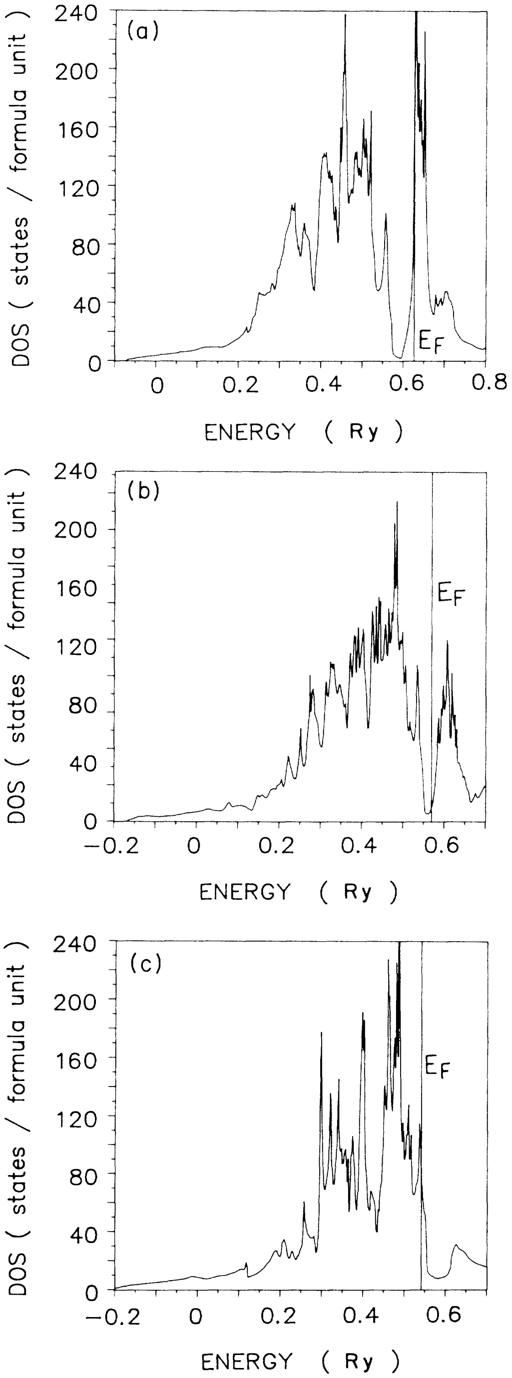

FIG. 5. Total density of states in the $L1_2$ structure: (a) Ni_3Al, (b) $Ni_3(Al,V)$, and (c) Ni_3V.

TABLE I. Equilibrium lattice constants (a and c), Wigner-Seitz radii (r_{WS}), bulk moduli (B), and heat of formation energies for Ni_3Al, Ni_3V, and $Ni_3(Al,V)$.

	a (Å)		c (Å)		r_{WS}	B (mbar)			Heat of
	Calc.	Expt.[a]	Calc.	Expt.[a]	(a.u.)	This work	Calc.[b]	Calc.[c]	formation[d] (kcal/mol)
$Ni_3Al(L1_2)$	3.55	3.56			2.622	2.0	2.1	2.1	44.5
$Ni_3V(D0_{22})$	3.54	3.542	7.21	7.213	2.629	2.4			21.3
$Ni_3(Al,V)$ $(L1_2)$	3.53		7.19		2.624	2.4			37.1
$(D0_{22})$	3.53		7.20		2.629	2.3			30.3

[a] Reference 12.

[b] Reference 10.

[c] Reference 13.

[d] The calculated heat of formation is the energy difference between the compound and the weighted sum of the constituents, i.e., $\Delta E = E_{M_a X_b} - (aE_M + bE_X)$.

these two structures (i.e., for the different site substitutions).

Figures 3 and 4 show the Ni d and V d partial density of states for $Ni_3(Al,V)$ in the $L1_2$- and $D0_{22}$-like structures, respectively. In these figures the nickel lattice sites are distinguished according to their individual environment (cf. Fig. 1) as three types: Ni atoms located in the same (001) plane as the Al or V atoms are called type 1 or type 3, respectively; the remainder are called type 2. It can be seen that the d-d hybridization between V and the host (Ni) appears in both the $L1_2$-like and $D0_{22}$-like structures; however, the d-d interactions exhibit different features for the $L1_2$-like and $D0_{22}$-like structures of $Ni_3(Al,V)$. The strong hybridization between Ni d and V d levels in the $Ni_3(Al,V)$ $L1_2$-like structure has a special prominent feature: a well-separated bonding and antibonding region. Note that it is also a noticeable common feature for the $L1_2$ structures of Ni_3Al, Ni_3V, and $Ni_3(Al,V)$ (Fig. 5). A deep valley separates the bonding and antibonding parts of the DOS. Obviously, the stability of the compound depends on the position of the Fermi level. It is expected that cubic Ni_3V, in which the Fermi level is located in the antibonding region, is an unstable compound and Ni_3Al will be a stable compound in the $L1_2$ structure, because the Fermi level lies in the bonding region of the density of states. For $Ni_3(Al,V)$ in the $L1_2$-like structure, there are enough valence electrons due to the V addition to bring the Fermi level to a position just below the antibonding d-d hybrid states. Thus the valence electrons fill all the bonding states and leave all the antibonding states empty; therefore, the strongest bonding effect occurs in $Ni_3(Al,V)$ in the $L1_2$-like structure. It is also expected, from the rigid-band assumption, that Ti, Zr, Hf, Nb, Ta, Si, and Ge will stabilize the $L1_2$ structure in Ni_3Al in much the same way as V, and possibly preferentially occupy Al sites.

The calculated equilibrium lattice constants and bulk modulus for $Ni_3(Al,V)$ are shown in Table I. For comparison, the values for Ni_3Al ($L1_2$ structure) and Ni_3V ($D0_{22}$ structure) are included. The lattice constants of Ni_3Al and Ni_3V are in good agreement with experiment,[13] and also the calculated bulk modulus of Ni_3Al agrees well with other calculations.[11,14] It is apparent that a slight hardening effect caused by V addition in Ni_3Al can be seen and it seems that the hardness increment agrees with the experimental measurement on a Ni–12.3% Al–2.2% V ternary alloy.[1,15]

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