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Structural and stability of B2 $FeCo_{1-X}V_X$ and $Fe_{1-X}CoV_X$ systems: Cluster expansion approach

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Abstract

Fe-Co alloys are considered good candidates for high-temperature applications due to their high saturation magnetisation and Curie temperature. However, these alloys show low levels of ductility at room temperature. In this study, cluster expansion was employed to probe the thermodynamic stability of the $FeCo_{1-X}V_X$ and $Fe_{1-X}CoV_X$ alloys. Ten new stable structures were found from both $FeCo_{1-X}V_X$ and $Fe_{1-X}CoV_X$ systems. Their stability was observed by deducing the heats of formation, and it was found that $VFeCo_2$ and VFe_2Co (P4/mmm) are the most thermodynamically stable phases. The results also showed that vanadium prefers the Co-site rather than the Fe-site substitution. The calculated Pugh's ratio and Poisson's ratio confirm that alloying with V effectively improved the ductility. It was also found that $VFeCo_2$, VFe_2Co, VFe_4Co_3 and FeCo showed a positive shear modulus condition of stability for the structures. The ternary addition of V in the FeCo system resulted in enhanced magnetic properties. Thus, ternary systems with vanadium addition enhance the ductility of the Fe-Co systems, and these alloys could be used to develop future magnets.

Keywords: Fe-Co alloys, Fe-Co-V alloys, Cluster expansion, Thermodynamic properties, Ductility

Methodology

Cluster expansion

All the Cluster Expansion (CE) calculations of the present work were done using the program package Universal Cluster-Expansion (UNCLE) (Lerch *et al.,* 2009) developed by the group of Muller. The code can perform a complete CE fit using a genetic algorithm and predict the ground states of systems containing up to three or more elements. UNCLE continues to increase the number of clusters included in the cluster expansion until the desired accuracy is achieved.

This method was used to determine the ground-state structure and thermodynamic properties of $Fe_{1-x}CoV_x$ and $FeCo_{1-x}V_x$ alloys. The fitness of every figure-set was evaluated using the cross-validation score (CVS), which quantifies the predictive accuracy of the figure-set for an unknown structure (van de Walle *et al.,* 2002). A CE can be considered accurate if the CVS is less than 5 eV. The UNCLE code is used as a script interface to the Vienna ab initio simulation package (VASP), which defines a parameter that automatically sets up the k-point mesh for similar systems used, namely, 0.2 k-spacing.

Total energy calculation

The total energy calculations were performed using the VASP code (Kresse and Hafner, 1993; Kresse and Furthmüller, 1996) based on density functional theory (DFT). The exchange-correlation interaction was treated with the generalised gradient approximation (GGA) (Kohn and Sham, 1965) of Perdew-Burke-Ernzerhof (PBE) (Perdew *et al.,* 1996). An energy cutoff of 500 eV was used for the plane-wave expansion of the electronic wave functions. The k-spacing of 0.2 was used according to Monkhorst and Pack grid for specified k-point sampling (Monkhorst and Pack, 1976). A full geometry optimisation was performed on ground-state structures where atom position, cell volume and cell shape were allowed to change. Elastic properties were calculated from optimised structures with a small strain of 0.004.

Results and discussion

Ground state structures

Figure 1 (a) and (b) show the results of formation energies $\Delta E_f(\sigma)$, which were used in the fitting of cluster expansion Hamiltonians. The cluster expansion generated 14 new structures for B2 $Fe_{1-x}CoV_x$ (Fe-site) and 16 new structures for B2 $FeCo_{1-x}V_x$ (Co-site). The cross-validation score (CVS) was used to examines the predictive power of the cluster expansion. The CVSs values were found to be 0.37 and 0.10 meV/pos for $Fe_{1-x}CoV_x$ and $FeCo_{1-x}V_x$, respectively, indicating good cluster expansions (since CVS < 5 meV). In Figure 1 (a) and (b), the green squares with a cross inside represent the structures, which are the most favourable within BCC-type lattice phases, which were predicted as ground-state structures in the previous CE runs and which were recalculated using DFT.

It is noted that all formation energies are negative and form the vertices on the lower boundary of the convex hull for both $Fe_{1-x}CoV_x$ and $FeCo_{1-x}V_x$ ordered structures. This behaviour suggests that the structures are thermodynamic stable. Furthermore, the ground state line predicted five (5) stable structures relative to the predicted formation energies for both $Fe_{1-x}CoV_x$ and $FeCo_{1-x}V_x$ alloys. Among the stable structures, $VFeCo_2$ (Co-site) and VFe_2Co (Fe-site) are the most thermodynamically stable structures due to the lowest ΔEf ($\Delta Ef < 0$) as compared to other structures. It can be deduced from the findings that V performs better when substituting on the Co-site

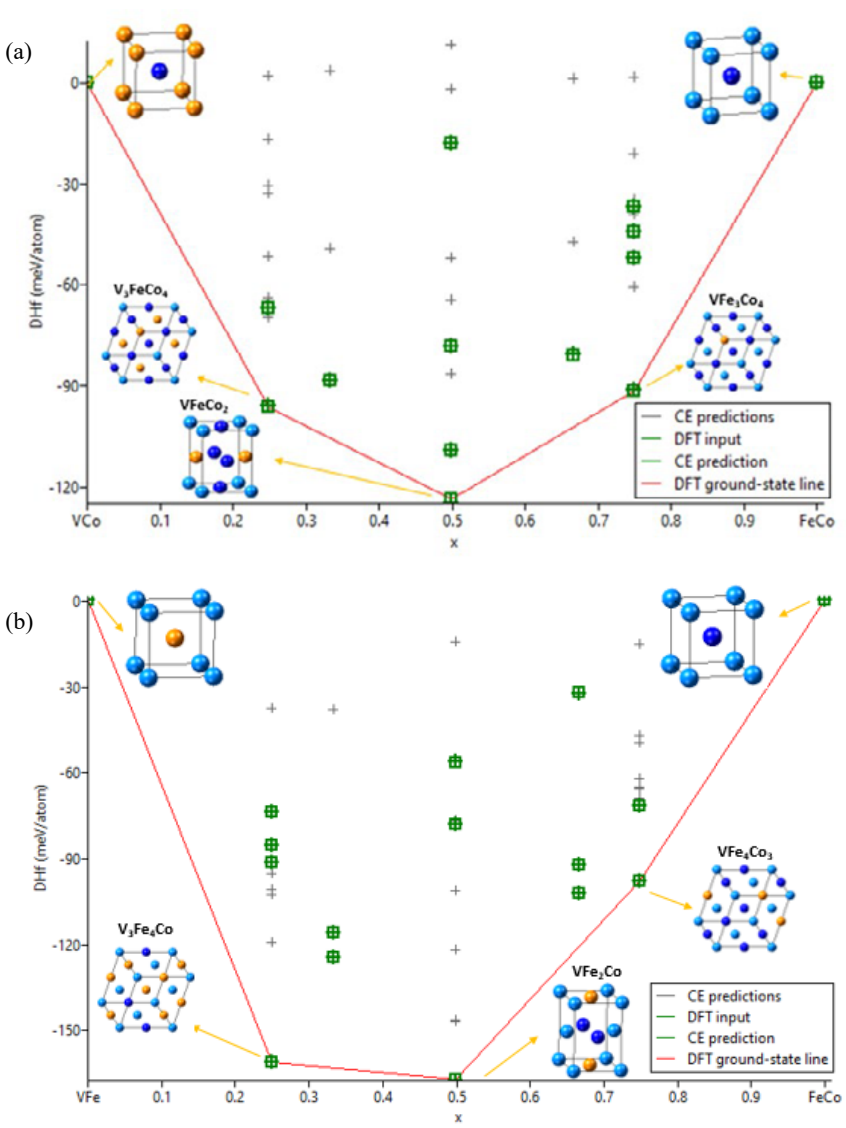

Figure 1: Ground state lines of the ternary B2 Fe-Co-V systems highlighting calculated enthalpy of formation values against V content, where (a) Fe-site substitution and (b) Co-site substitution

as the structures are more thermodynamically stable as compared to Fe-site.

Structural and thermodynamic properties

The space groups, equilibrium lattice parameters (a, b, c) and heats of formation of B2 $Fe_{1-x}CoV_x$ and $FeCo_{1-x}V_x$ structures are shown in Table 1. The binary systems, such as $Fe_{50}Co_{50}$, $V_{50}Fe_{50}$, and $V_{50}Co_{50}$ with a space group of Pm-3m, gave equilibrium lattice parameters 2.841 Å (2.840 Å) (Hasegawa *et al.,* 2019), 2.870 Å (2.910 Å) (Clavero *et al.,* 2006), and 2.886 Å, respectively. The result obtained is in good agreement with the theoretical values (in parenthesis) to within a 4 % error.

The heats of formation (ΔH_f) *is* estimated by the following expression:

$$\Delta H_f = E_C - \sum_i x_i E_i \qquad (1)$$

where E_C is the calculated total energy of the compound and E_i is the calculated total energy of the element in the compound. The most stable structures are $VFeCo_2$ (Co-site) and Fe_2CoV (Fe-site), with the lowest heats of formation of -0.226 and -0.222 eV/atom, respectively.

Elastic properties

Elastic constants are important parameters, which can be used to predict the mechanical stability of the material. They can differ depending on the lattice type, *i.e.,* for the cubic and tetragonal, there are three (c_{11}, c_{12}, c_{44}) and six (c_{11}, c_{12}, c_{13}, c_{33}, c_{44}, c_{66}) independent elastic constants, respectively. The stability criterion for cubic crystal structures (Wang *et al.,* 2006) is as follows:

Table 1: The predicted space groups, lattice parameters (a, b, c) and heats of formation of $Fe_{1-x}CoV_x$ and $FeCo_{1-x}V_x$ alloys

Structure	Space group	a(Å)	b(Å)	c(Å)	ΔH_f (eV/atom)
			$Fe_{1-x}CoV_x$		
VCo	Pm-3m	2.886	2.886	2.886	-0.192
V_3FeCo_4	Im-3m	2.467	2.467	2.467	-0.067
$VFeCo_2$	P4/mmm	3.533	3.494	3.494	-0.226
VFe_3Co_4	Im-3m	2.467	2.467	2.467	-0.107
FeCo	Pm-3m	2.841	2.841	2.841	-0.140 (-0.51 (Wu D, et al, 2008), -0.065 (Fu C L and Maja Krcmar, 2006))
			$FeCo_{1-x}V_x$		
VFe	Pm-3m	2.870	2.870	2.870	-0.330
V_3Fe_4Co	Im-3m	2.444	2.444	2.444	-0.201
VFe_2Co	P4/mmm	3.052	3.882	3.882	-0.222
VFe_4Co_3	Im-3m	2.468	2.468	2.468	-0.164
FeCo	Pm-3m	2.841	2.841	2.841	-0.140

$$c_{11} > c_{12}, c_{44} > 0, \text{and } c_{11} + 2c_{12} > 0, \qquad (2)$$

As for tetragonal crystal stability, the criterion (Mehl and Klein, 1994) is as follows:

$$c > 0, c_{66} > 0, c_{11} > |c_{12}| \text{ and } c_{11}+c_{12} - \frac{2c_{13}^2}{c_{33}} > 0, \qquad (3)$$

The stability criterion for the elastic constants must be satisfied for a structure to be considered stable. A positive elastic Shear modulus, C' ($(1/2(c_{11}-c_{12})>0$) shows the mechanical stability of a lattice structure, otherwise, it is unstable. In Table 2, the calculated elastic properties, Pugh's and Poisson's ratios of the $Fe_{1-x}CoV_x$ and $FeCo_{1-x}V_x$ alloys are shown. In the case of $Fe_{1-x}CoV_x$, it is notable that the mechanical stability conditions are satisfied for all calculated structures due to positive C' values except for VCo. For $FeCo_{1-x}V_x$, it is noted that only V_3Fe_4Co is mechanically unstable displaying negative c_{12}, c_{44} and C', which does not satisfy the cubic stability criteria.

Furthermore, we calculated the ratios of Bulk to Shear modulus (B/G) and Poisson's (σ) to investigate the ductility of the structures. Pugh (1954) proposed that materials are predicted to show ductile behaviour if the value of the Pugh ′s criterion B/G 1.75. All the structures satisfy the ductility conditions since B/G values are greater than 1.75, except for VCo. Note that the structure is considered as ductile when σ is greater than 0.26 otherwise brittle (Frantsevich *et al.,* 1982). The σ values were found to be greater than 0.26 for all set of structures, except for VCo.

Conclusions

Employing the cluster expansion method, we have successfully studied the ground state structures and thermodynamic properties of $Fe_{1-x}CoV_x$ and $FeCo_{1-x}V_x$ alloys. The cluster expansion method has successfully generated 14 new structures on B2 $Fe_{1-x}CoV_x$ (Fe-site) and 16 new structures for B2 $FeCo_{1-x}V_x$ (Co-site). All the heats of formation were negative, showing no tendency of phase separations for both systems. $VFeCo_2$ and VFe_2Co (P4/mmm) are the most thermodynamically stable phases with the lowest formation energies. The ductility is improved due to an increased tendency in the Pugh (B/G), and Poisson ′s ratio. The findings revealed that V prefers substituting on the Co-site than the Fe-site in agreement with the predicted heats of formation. The findings suggest that $Fe_{1-x}CoV_x$ and $FeCo_{1-x}V_x$ alloys could be used in the design of future magnets.

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Table 2: Elastic constants (GPa), Pugh's (B/G) and Poisson's () ratios of $Fe_{1-x}CoV_x$ and $FeCo_{1-x}V_x$ alloys

Structure	C_{11}	C_{12}	C_{44}	C_{13}	C_{33}	C_{66}	C'	B/G	σ
$Fe_{1-x}CoV_x$									
VCo	84.01	287.52	89.97				-101.76	1.079	0.146
V_3FeCo_4	1036.02	669.29	70.93				183.37	8.191	0.441
$VFeCo_2$	386.65	188.04	201.56	187.69	359.00	191.96	99.31	1.793	0.264
VFe_3Co_4	333.65	108.23	83.74				112.71	2.981	0.349
FeCo	311.54	163.35	129.57				74.10	2.162	0.299
$FeCo_{1-x}V_x$									
VFe	275.87	167.00	64.60				54.44	3.377	0.365
V_3Fe_4Co	480.16	-30.74	-23.66				255.45	3.421	0.366
VFe_2Co	222.83	191.44	58.45	191.49	303.35	114.75	15.70	3.201	0.358
VFe_4Co_3	309.27	88.01	89.41				110.63	2.176	0.300
FeCo	311.54	163.35	129.57				74.10	2.165	0.299

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