The effect of vanadium on the magnetic and mechanical properties of B2 FeCo alloy: a DFT approach

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Dates:
Received: 7 Sept. 2020
Revised: 5 Aug. 2022
Accepted: Feb. 2023
Published: May 2024

How to cite:
Ledwaba, T.M., Diale, R.G., Ngoepe, P.E., and Chauke, H.R. 2024. The effect of vanadium on the magnetic and mechanical properties of B2 FeCo alloy: a DFT approach. *Journal of the Southern African Institute of Mining and Metallurgy*, vol. 124, no. 5. pp. 263–268

DOI ID:
http://dx.doi.org/10.17159/2411-9717/1368/2024

Abstract

FeCo alloys play an important role in soft magnetic materials with a wide range of technological applications due to their high saturation magnetization and Curie temperature. However, these alloys have low ductility at room temperature. The ductility can be improved by the ternary addition of elements such as V. A density functional theory supercell approach was used to generate B2 $Fe_{50}Co_{50-x}V_x$ ($0 \leq x \leq 50$) structures and the properties were evaluated at different atomic percentage compositions to determine the ductility at room temperature. The structures were fully optimized to obtain better equilibrium ground-state properties such as lattice parameters and thermodynamic properties for both binary and ternary systems. The stability of $Fe_{50}Co_{50-x}V_x$ was evaluated from the heats of formation, elastic properties, and phonon dispersion curves. Furthermore, magnetic strength was evaluated from magnetic moments. It was found that all structures are thermodynamically stable due to the negative heats of formation. The calculated Pugh's ratio and Poisson's ratio confirm that alloying with V effectively improved the ductility. It was also found that $Fe_{50}Co_{50-x}V_x$ showed a positive shear modulus for the entire concentration range investigated, in agreement with phonon dispersion curves. The ternary addition of V to the FeCo system resulted in reduced magnetic strength due to a decrease in magnetic moments. These findings reveal that B2 FeCo-V alloys can be used as components and actuators for the automotive industry.

Keywords

FeCo alloy, magnetic properties, phonons, ductility

Introduction

FeCo alloys are relatively soft materials that are used in various engineering applications owing to their superior properties, particularly their high saturation magnetization (Liu and Morisako, 2008). FeCo possesses improved properties such as high mechanical strength and soft magnetic character, with high permeability, a high Curie temperature, high tensile strength, and the highest saturation magnetization of all known magnetic alloys, which are required for advanced power applications (Sides, Kassouf, and Huang, 2019). However, B2 FeCo suffers from low ductility at room temperature, which makes this alloy difficult to process (Sourmail, 2005). Furthermore, the current FeCo alloys cannot withstand temperatures above the transformation temperature for lenghty periods. which limits their use in the aerospace industry (Horwath. Turgut, and Fingers, 2006). Due to their smooth magnetic characteristics at elevated temperatures, there is a long tradition of using FeCo alloys with ternary element additions as engineering materials.

Various attempts to improve the ductility of FeCo alloys through ternary additions have been reported, but most did not yield the required properties. However, Pd, V, Ti, Ta, and Cr have shown promise (Liu, 2011). Vanadium additions impart higher tensile strength and elongation at room temperature (Albaaji, 2017). By combining the soft magnetic properties of iron and hard magnetic properties of cobalt and vanadium, an optimal magnetic material could be developed. In a previous investigation (Ledwaba et al., 2021), density functional theory (DFT) was used together with cluster expansion to investigate the possible structures that can be formed in Fe-Co-V ternary alloys. 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, leading to improved ductility. In this investigation, the ternary alloying of FeCo with V was performed using the DFT approach to investigate the thermodynamic, mechanical, and magnetic stability. It was found that the addition of V to B2 FeCo resulted in improved thermodynamic and mechanical properties. Figure 1 shows the atomic arrangement of the investigated structures (B2 FeCo and FeCo-V).

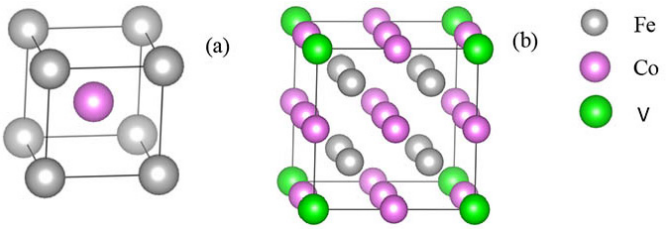

Figure 1—The atomic arrangements of (a) B2 FeCo and (b) B2 FeCo-V (2 × 2 × 2 supercell) with the space group Pm-3m

Methodology

The calculations were performed using the Vienna *ab-initio* simulation package (VASP) code based on DFT (Kresse and Hafner, 1993; Kresse and Furthmuller, 1996). The interaction between the core and the valence electrons was described using the projector augmented wave (PAW) method. The generalized gradient approximation (GGA) of the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional (Perdew, Burke, and Ernzerhof, 1996) was employed. An energy cut-off of 500 eV was used to converge the total energy of the structures. A k-spacing of 0.2 was used for FeCo and equivalent numbers of k-points were used for the supercell, following Monkhorst and Pack (1976). The calculations were carried out using a 2 × 2 × 2 supercell with 16 atoms. The substitutional search tool in VASP was used to substitute Co with V at different atomic percentage compositions. The elastic constants were calculated for a small strain of 0.005 for all structures. The phonon dispersion curves were calculated using PHONON code (Parlinski, Li, and Kawazoe, 1997) as implemented in Materials Design within the MedeA software platform.

Results and discussion

Structural and thermodynamic properties

Figure 2 depicts the equilibrium lattice constants for the binary $Fe_{50}Co_{50}$ and ternary $Fe_{50}Co_{50-x}V_x$ ($0 \le x \le 50$) alloys. It was found that the lattice constant of $Fe_{50}Co_{50}$ is 2.844 Å, which compares well with the experimental value of 2.843 Å (Materials Explorer, 2020), a difference of 0.035%. The lattice parameters were determined from fully relaxed structures; both the lattice geometry and ionic positions were fully optimized. It is clear that the equilibrium lattice parameter of $Fe_{50}Co_{50-x}V_x$ increases as the V content is increased. This is due to the large atomic radius of V (135 pm) compared to Co (125 pm). The thermodynamic stability of $Fe_{50}Co_{50-x}V_x$ is predicted from calculated heats of formation (ΔH_f) using the following expression:

$$\Delta H_f = E_C - \sum_i x_i E_i \quad [1]$$

where E_C is the calculated total energy of the compound and E_i is the calculated total energy of elements in the compound. For a structure to be thermodynamically stable, the heat of formation must have the lowest negative value ($\Delta H_f < 0$) – a positive value implies instability. Figure 3 presents the heats of formation for the B2 $Fe_{50}Co_{50-x}V_x$ systems for concentrations $0 \le x \le 50$. The heat of formation for the binary B2 $Fe_{50}Co_{50}$ was found to be –0.057 eV per atom, which is in good agreement with an experimental value of –0.065 eV per atom obtained by Fu (2006), within 3%. As shown, the ΔH_f decreases as V content is increased, implying that the structure becomes thermodynamically stable with the addition of V.

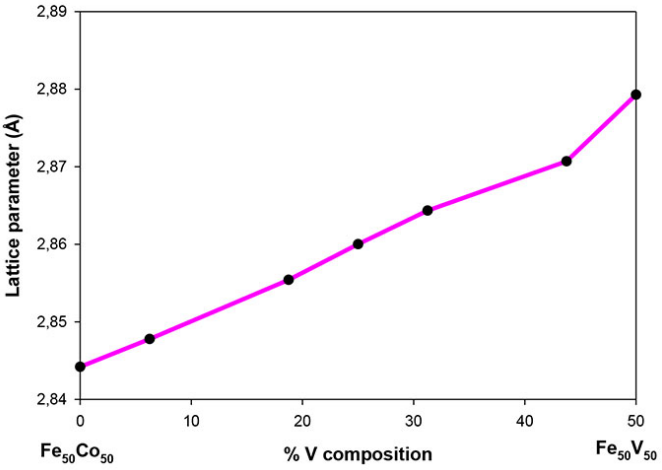

Figure 2—Lattice parameter (Å) *versus* atomic per cent V (at.% V), where 0 ≤ x ≤ 50

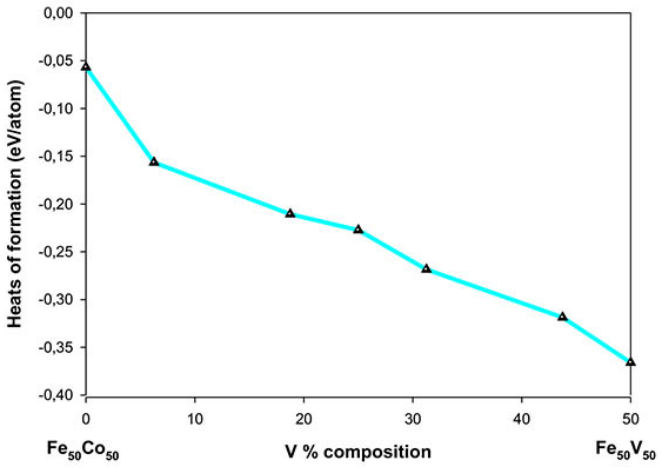

Figure 3—Heat of formation (ΔH_f) versus atomic per cent V for $Fe_{50}Co_{50-x}V$, where $0 \le x \le 50$

Elastic constants

The elastic properties give important information about the mechanical stability of compounds. For the cubic symmetry B2 crystal structure of $Fe_{50}Co_{50-x}V_x$, there are three independent elastic constants (C_{11}, C_{12}, and C_{44}). The stability criterion for cubic crystals (Wang et al., 1993) is as follows:

$$C_{11} > C_{12}, C_{44} > 0, \text{and } C_{11} + 2C_{12} > 0, \quad [2]$$

where the shear modulus C' can be calculated as:

$$C' = \frac{1}{2}(C_{11} - C_{12}) \quad [3]$$

In Figure 4, the calculated elastic properties of the $Fe_{50}Co_{50-x}V_x$ alloys where ($0 \le x \le 50$) are shown. The stability criterion for the elastic constants must be satisfied for the structure to be stable. A positive shear modulus, C' shows that a crystal is mechanically stable; a negative C' indicates instability. It is notable that the mechanical stability conditions are satisfied for the entire concentration range of $Fe_{50}Co_{50-x}V_x$ alloys where ($0 \le x \le 50$).

Figure 5a shows the variations in bulk, shear, and Young's moduli with atomic per cent V. The bulk modulus decreasees with increasing V concentration below 31 at.% and increases above this

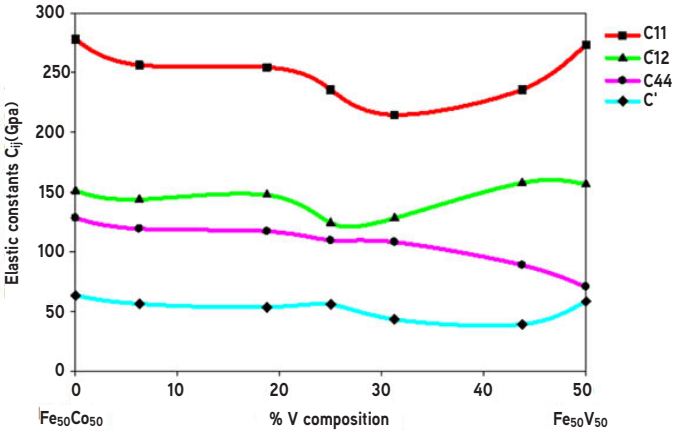

Figure 4—Elastic constants (GPa) versus atomic per cent V for $Fe_{50}Co5_{0-x}V_x$, where 0 ≤ x ≤ 50

value. This indicates that the compressibility of the $Fe_{50}Co_{50-x}V_x$ alloys is enhanced above 31 at.% V. $Fe_{50}Co_{43.75}V_{6.25}$ appears to have the highest bulk modulus (184.96 GPa). The shear modulus and Young's modulus decrease minimally with an increase in V concentration over the entire compositional range. $Fe_{50}V_{50}$ appears to be more compressible, as suggested by lowest shear modulus. Young modulus was calculated to check the rigidity of the material. The highest Young's modulus is regarded as indicating high stiffness. It is noted that $Fe_{50}Co_{43.75}V_{6.25}$ has the highest Young's modulus of all the compositions investigated.

To assess the ductility of the material with different atomic compositions of V, the Cauchy pressure, Poisson's ratio, and B/G ratio (bulk modulus/shear modulus) were determined as shown in Figures 5b, 5c, and 5d, respectively. The Cauchy pressure of a cubic crystal is calculated as (C_{12}-C_{44}) for the (100) plane. A positive Cauchy pressure indicates an ionic character and ductile behaviour, while a negative value indicates a weak covalent bond and brittle behaviour (Pettfor, 1992). As the concentration of V is increased, the Cauchy pressure values remain positive for the entire range ($0 \leq xx \leq 50$), suggesting that the system is ductile at room temperature (see Figure 5b). Poisson's ratio (σ) was also evaluated to confirm the ductility of the materials. Note that the structure is considered ductile when σ is greater than 0.26, otherwise brittle (Frantsevich and Voronov, 1983). As the content of V is increased, the σ values were found to be greater than 0.26 in the entire concentration range, indicaring a condition of ductility (Figure 5c).

Considering that the shear modulus characterizes the resistance to plastic deformation and the bulk modulus the resistance to fracture (Mayer et al., 2003) the Pugh ratio B/G was calculated and evaluated to determine the ductility and brittleness of the structures. The structures (see Figure 5d) were observed to be ductile since all the ratios were greater than the critical value of 1.75 (Pugh, 1954).

Figure 6a shows the magnetic moments of the $Fe_{50}Co_{50-x}V_x$ alloys ($0 \leq x \leq 50$). The magnetic moment indicates the magnetic strength and orientation of a magnet. It is noted that the magnetic moment decreases at 6.25 at.% V. However, above 6.25 at.% V the reduction in magnetic moments is minimal. This suggests that the addition of V on $Fe_{50}Co_{50}$ slightly reduces the magnetic moment.

Phonon dispersion curves

To investigate the vibrational stability of the B2 $Fe_{50}Co_{50-x}V_x$ alloys, we determined the phonon dispersion curves presented in Figure 7. The calculations were carried out using the PHONON code (Parlinski, Li, and Kawazoe, 1997). A structure is considered vibrationally stable if there are no soft modes along with negative directions in the Brillouin zone. The absence of soft modes in all directions indicates that the phonon dispersion curves of B2 $Fe_{50}Co5_{0-lyx}V_x$ are vibrationally stable below 43.75 at.% V. This prediction is consistent with the elastic moduli (Figure 4). However,

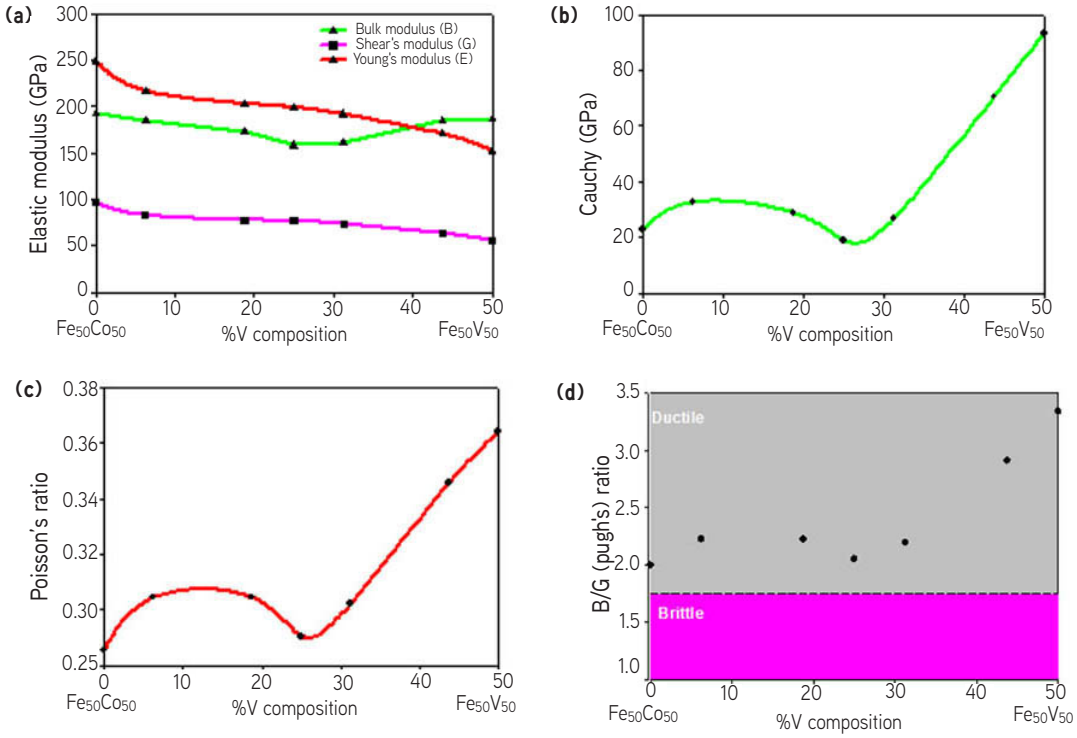

Figure 5—(a) Elastic moduli, (b) Cauchy pressure, (c) Poisson's ratio, and (d) B/G ratio against atomic per cent V for $Fe_{50}Co_{50-x}V_x$ where 0 ≤ x ≤ 50

$Fe_{50}V_{50}$ displays negative vibrations along the M and X directions, which does not imply mechanical instability but rather shows the potential to undergo a phase transition from high to lower temperature phases, hence the presence of soft modes.

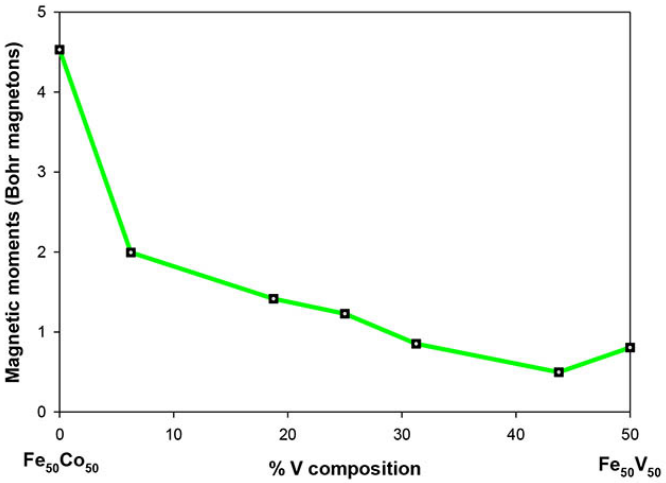

Figure 6—(a) Magnetic moments (Bohr magnetons) versus atomic per cent V for $Fe_{50}Co_{50-x}V_x$, where $0 \leq x \leq 50$

Conclusions

The *ab-initio* DFT approach was successfully used to study the effect of V content on the structural, magnetic, and mechanical properties of B2 FeCo alloy. The results showed that $Fe_{50}Co_{50-x}V_x$ is thermodynamically stable at high concentration of V with the lowest heats of formation. It was found that $Fe_{50}Co_{50-x}V_x$ alloys are mechanically stable for the entire concentration range studied. The bulk modulus (B), shear modulus (G), and Young's modulus (E) showed a decreasing tendency with increasing V content. The ductility improved as shown by the increases in the Pugh ratio (B/G), Cauchy pressure (C_{12}-C_{44}), and Poisson's ratio with an increase in V concentration. The magnetic moment was found to decrease with the addition of V, indicating a lower magnetic strength. The phonon dispersion curves showed mechanical stability over the entire concentration range studied, except for $Fe_{50}V_{50}$. The findings may provide guidance to the future development of ferromagnets made from new $Fe_{50}Co_{50-x}V_x$ alloys.

Acknowledgements

The computing resources provided by the Materials Modelling Centre (MMC) at the University of Limpopo and Center for High Performance Computing (CHPC) are deeply appreciated. We

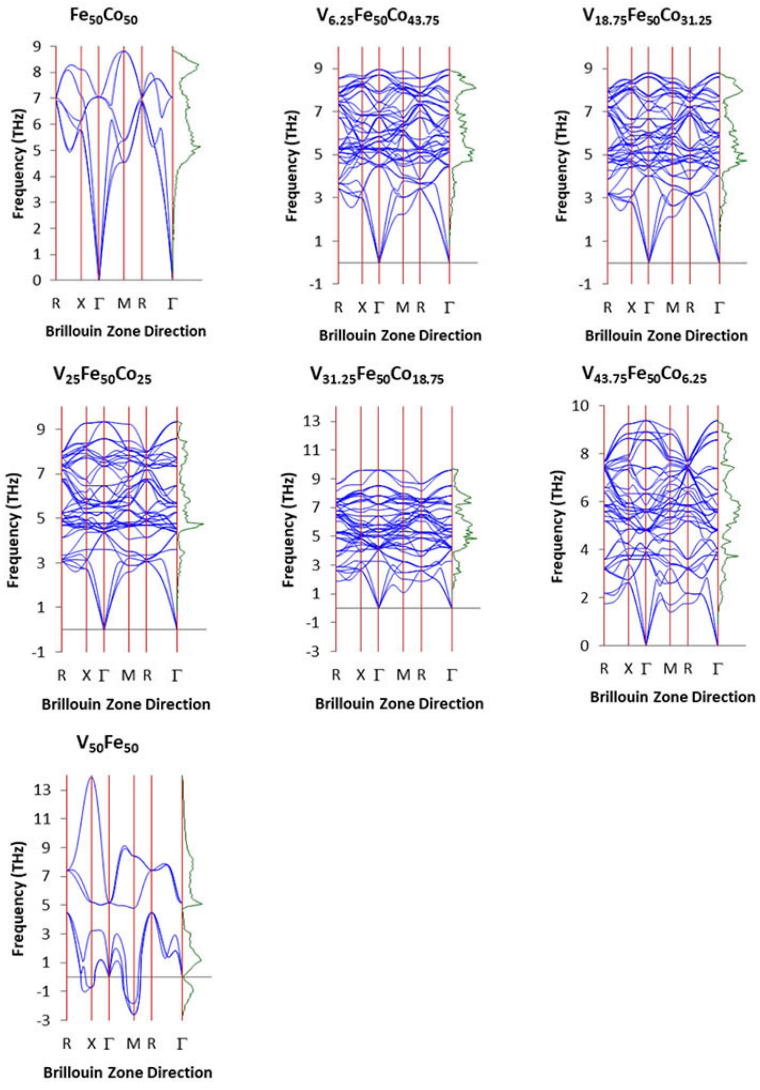

Figure 7—Phonon dispersion curves for B2 $Fe_{50}Co_{50-x}V_x$ alloys, where $0 \leq x \leq 50$ and the Γ (000) denote the centre of the Brillouin zone

gratefully acknowledgs The support of the South African Research Chair Initiative of the Department of Science and Technology.

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