Thermodynamic stability of doped FeAl-X \((X = \text{Pd, Ag, Pt and Ru})\) systems

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Abstract. Iron-aluminides based systems play a significant role in many industrial applications due to their excellent resistance to oxidation at high temperatures. In particular, these alloys are applicable as thermocouples. In this paper, we used first-principles density functional theory to investigate the stability of FeAl and ternary FeAl-X alloys. Their equilibrium lattice parameters are in better agreement to within 2% with the experimental data. We employed virtual crystal approximation and supercell approaches to model various atomic compositions at \(0 \leq x \leq 1\) for Ag, Pt, Pd and Ru. Their thermodynamic, electronic and mechanical properties were deduced from their equilibrium lattice constants. It was found that the addition of Ag, Pt, Pd and Ru enhances the stability at lower atomic percentage composition. It was found that Ag and Pd stabilizes the FeAl-X to lower percentage compositions. Furthermore, their heats of formation, density of states and elastic constants gave essential agreement to describe the structural, thermodynamic and mechanical stability of these systems.

1. Introduction
Iron-aluminides based alloys have created a great amount of interest due to their potential as candidates for applications in the energy sector, such as boilers and pipes. In order to improve the strength and ductility of the Fe-Al alloys various steps are considered, which included the addition of third metals such as Pt, Ru, Pd, Ag [1]. Previous reports showed that the presence of these elements increases the hardness of the alloys slightly [2]. Furthermore, addition of small amounts increased the corrosion resistance, though these alloys suffer limited ductility room temperature at 873 K [3]. Sharma et al demonstrated that the addition of Pt, Ru, Ag and Pd increases the resistance to tarnishing or the formation of silver sulphide [4].

Other work investigated the Fe40-Al alloy with addition of Ag, Ru, Pt and Pd for small concentrations of either 0.2 at. % or 0.5 at. %. On the other hand, studies had illustrated the hot corrosion behavior of Fe40-Al intermetallic alloyed with 2.5 at. % Ag at 723 K. Addition of Ag on Fe40-Al alloy enhances the corrosion behavior, particularly when the alloy was exposed to molten salt mixture at 943 K [5]. The binary Fe40-Al alloy exhibit a more active corrosion potential but at lower corrosion rate. The ternary FeAl-Ag alloy exhibited a more noble corrosion potential but a bigger corrosion rate. This behavior is due to the formation of a layer of corrosion products composed mainly by a mixture of Al and Fe protective oxides and other compounds such as metals chlorides [5] [6].

In this paper we employed density functional theory (DFT) to investigate the mechanical, thermodynamic and electronic properties of Pd, Pt, Ag and Ru doped on B2 FeAl intermetallic. A
combination of ab-initio and molecular dynamics approach [4] were used to investigate the influence of ternary addition. The Heats of formation revealed stability for Pd and Ru addition at 0.2 at. %; while Ag and Pt at 0.5 at. % composition in agreement with the experimental data. The elastic constants were also calculated to describe the mechanical stability for the FeAl-X systems for small concentrations \(0 \leq x \leq 1\), and were found to be in accordance with the experimental findings [7]. The temperature dependence showed that Ru and Ag are stable over a wide range of temperature below 1000 K.

2. Methodology

Density functional theory (DFT) [8] within the generalized gradient approximation (GGA) by Perdew, Burke and Ernzerhof (PBE) [9] was used to study the FeAl-X alloys. We employed the plane wave pseudopotential method as implemented in CASTEP code [10, 11]. An energy cut-off of 500 eV was used, as it was sufficient to converge the total energy of the B2 FeAl phase. The Brillouin zone integrations were performed for suitably large sets of k-points of 10 X 10 X 10 according to Monkhorst and Pack [12] before and after doping.

The minimum and maximum Guassian smearing width were respectively set at 0.4 and 0.1 eV for the FeAl-Ag/Pd structures. For the exchange-correlation functional, the GGA-PBE was chosen. In the calculation of elastic constants and density of states, sufficient number of k-points were used. Optimization of structural parameters (atomic positions and lattice parameters) was achieved by minimization of forces and stress tensors. Initially, the optimised binary FeAl structures gave equilibrium lattice parameter with better agreement to the experimental findings. The incorporation of Pt, Pd, Ru and Ag as dopants in FeAl was achieved using virtual crystal approximation (VCA) [13]. The Dmol3 code was used to perform the temperature dependence calculations. A time step of 16ps and NVE ensemble was used to determine the transition temperature of FeAl-X systems.

3. Results and discussion

3.1. Thermodynamic stability

The heats of formation \(\Delta H_f\) of the Fe\(_{50-x}\)Al\(_{50}\)-X is calculated as:

\[
\Delta H_f = \frac{1}{N} [E^{FeAl} - \{(1-x)E^{Fe} + xE^{Al}\}]
\]

| Compositions    | Dopant (at. %) | Lattice parameter (Å) | Volume (Å\(^3\)/atom) | \(\Delta H_f\) (eV/atom) |
|-----------------|----------------|------------------------|-------------------------|--------------------------|
| Fe\(_{50}\)Al\(_{50}\) | -              | 2.852                  | 23.192                  | -0.5680 (-0.605) [14]   |
| Fe\(_{49.8}\)Al\(_{50}\)Pd\(_{0.2}\) | 0.2            | 2.276                  | 9.077                   | -0.243                   |
| Fe\(_{49.5}\)Al\(_{50}\)Ag\(_{0.5}\) | 0.5            | 2.264                  | 8.931                   | -0.244                   |

Table 1. Heats of formation \(\Delta H_f\) of FeAl and doped FeAl-Pd/Ag structures.

Figure 1 shows the heats of formation \(\Delta H_f\) against atomic composition for FeAl-X structures doped with Pd, Ag, Ru and Pt atoms, \(\Delta H_f\) are listed in Table 1. The solid common-tangent line was constructed to illustrate the ground state structures of their different phase composition. Among the structures considered, the most favourable intermetallic phases was found to be Fe\(_{49.8}\)Al\(_{50}\)Ru\(_{0.2}\), Fe\(_{49.5}\)Al\(_{50}\)Ag\(_{0.5}\) and Fe\(_{49.8}\)Al\(_{50}\)Pd\(_{0.2}\) with the lowest heats of formation [7]. Figure 1 (d) shows that at 0.35, 0.38, 0.45 and 0.48 at. % Pt may be considered meta-stable. However, we also note that figure 1 (b) points that 0.3, 0.4, 0.6 and 0.7 at. % may be considered as meta-stable phases since they fall above
the stability tangent line. These phases have not been reported in literature. The dotted straight line show that the ΔH increases as the Ag concentration is increased, implying that the stability decreases. However, it is clear that at 0.5 at. % Ag, the structure becomes the most stable in agreement with experimental findings [7].

3.2. Mechanical Properties of Fe50-XAl50X (X= Pt, Pd, Ru, Ag)

In order to investigate the elastic stability of the ternary systems, we calculated the elastic constants (C_{ij}) for Fe_{49.80}Al_{50}Pd_{0.2}, Fe_{49.50}Al_{50}Ag_{0.5}, Fe_{49.50}Al_{50}Pt_{0.5} and Fe_{49.80}Al_{50}Ru_{0.2} systems at different concentrations as shown in table 2. Note that the symmetry was unchanged during doping, and thus three independent elastic constants (C_{11}, C_{12}, and C_{44}) have been found for the cubic lattice. The stability conditions for cubic lattice are:

C_{11} > 0, C_{11} - C_{12} > 0; C_{11} + 2C_{12} > 0; C_{44} > 0

We observed that all independent elastic constants are positive and satisfy the stability conditions for Ru doped. Furthermore, the calculated shear moduli is positive (C' > 0) indicating that the structure is elastically stable (see figure 2 (a)). The elastic constants in figure 2(b) confirmed instability at 0.3 at. % Pt, while Figure 2 (c) shows that C' is positive below 0.5 at. % Pd (condition of stability). However,
the structure shows negative behavior (instability) above 0.5 at. % Pd. The elastic stability criteria for ductility and brittleness as proposed by Pugh was used (where \( B/G < 1.75 \) is for brittleness or \( B/G > 1.75 \) is for ductility) [15]. In this case, the predicted \( B/G \) ratio for Pd and Ag are greater than 1.75 (indicating ductility), while those for Ru and Pt are less than 1.75 (brittleness).

| Structures        | \( C_{11} \) (GPa) | \( C_{12} \) (GPa) | \( C_{44} \) (GPa) | \( C' \) (GPa) | \( B \) (GPa) | \( G \) (GPa) | \( B/G \) (GPa) |
|-------------------|---------------------|---------------------|---------------------|----------------|---------------|---------------|----------------|
| \( \text{Fe}_{49.80}\text{Al}_{50}\text{Pd}_{0.2} \) | 149.6               | 89.5                | 16.4                | 30.1           | 18.5          | 7.1           | 2.57           |
| \( \text{Fe}_{49.50}\text{Al}_{50}\text{Ag}_{0.5} \) | -1.3                | -15.4               | -16.6               | 7.1            | 48.6          | 10.7          | 4.50           |
| \( \text{Fe}_{49.80}\text{Al}_{50}\text{Ru}_{0.2} \) | 279.4               | 140.6               | 147.4               | 69.4           | 186.9         | 108.9         | 1.72           |
| \( \text{Fe}_{49.50}\text{Al}_{50}\text{Pt}_{0.5} \) | 278.9               | 139.9               | 147.5               | 208.9          | 186.2         | 101.8         | 1.707          |

Figure 2. The elastic constants (GPa) for the (a) \( \text{Fe}_{50-x}\text{Al}_{50}\text{Pt}_x \), (b) \( \text{Fe}_{50-x}\text{Al}_{50}\text{Ru}_x \) and (c) \( \text{Fe}_{50-x}\text{Al}_{50}\text{Pd}_x \) structures.

3.3. Density of states

Figure 3 shows the partial and total density of states of Pd and Ag doped FeAl systems. These systems display similar total DOS characterized by a strong \( d \)-orbital peak at \( E_f \) (\( E-E_f = 0 \)). We see that the
Fermi level hits the top of the d- peak in both cases, while to that of Pd doped DOS is broader (figure 3(a)). The peak is due to the strong contribution of the 4d- orbital with less contribution of the s- and p- orbital. This signifies electronic stability which is in good agreement with the predicted heats of formation. The small sharp peak at about 0.5 eV (figure 3 (b)) emanates from hybridization of the 4d-orbitals (Fe, Ag) and 2p- orbital.

![Figure 3](image)

**Figure 3.** Total and partial density of states of ternary systems (a) Fe<sub>49.80</sub>Al<sub>50</sub>Pd<sub>0.2</sub> and (b) Fe<sub>49.50</sub>Al<sub>50</sub>Ag<sub>0.5</sub>, with the Fermi energy taken as energy zero (E-E<sub>f</sub> = 0).

### 3.4. Effect of temperature on FeAl and FeAl-Pd/Ru/Ag.

The results obtained showed preferential doping on the Fe sub-lattice with Pt and Ru being the most favourable dopant than Ag and Pd. According to literature, the binary FeAl have limited room temperature above 873 K [16]. In this study, we note from the binding energy curves that the binary Fe<sub>50</sub>Al<sub>50</sub> phase is stable up to 900 K and becomes less stable above this temperature being in agreement with the experimental. However, the addition of 0.2 at. % Ru showed higher transition temperature of 1000 K, slightly lower for Ag (900 K), as compared to the experimental value of 1273 K and 1073 K [17, 18] and shows to be worse for Pd (400 K). The Ru and Ag doped systems shows a sudden jump at 1000 K and 900 K, respectively, which implies that the system is unstable above this temperature range.
4. Summary and conclusion
The DFT results were in good agreement with the experimental findings [7]. It was found that the Fe\textsubscript{50}Al\textsubscript{50} structure was more stable (lowest heats of formation) and VCA showed preference of doping on Fe than Al sublattices: Fe\textsubscript{48.50}Al\textsubscript{51.50}Ag\textsubscript{0.5}, Fe\textsubscript{48.80}Al\textsubscript{50}Pd\textsubscript{0.2}, Fe\textsubscript{48.50}Al\textsubscript{50}Pt\textsubscript{0.5} and Fe\textsubscript{49.80}Al\textsubscript{50}Ru\textsubscript{0.2}. The equilibrium heats of formation, lattice parameters, elastic properties, density of states and temperature effect on the B2 FeAl phase were determined using \textit{ab initio} calculations. Interestingly, the B2 Fe\textsubscript{50}Al\textsubscript{50} was found to be energetically and mechanically stable over the other phases at different compositions. These phases exist in the range between 50 and 100 atomic percent Al of the experimental phase diagram [19]. The shear modulus (C') of the B2 Fe\textsubscript{50}Al\textsubscript{50} and Fe\textsubscript{49.80}Al\textsubscript{50}Ru\textsubscript{0.2} phases are found to be positive, satisfying the condition of stability, whereas for Fe\textsubscript{48.50}Al\textsubscript{50}Pt\textsubscript{0.5}, the C' showed condition of instability at 0.3 at. %.

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