

FIRST-PRINCIPLES STUDY OF INTERFACE ENERGIES IN Fe-Al-BASED SUPERALLOY NANOCOMPOSITES

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Abstract

Fe-Al-based nanocomposites with a superalloy-type of microstructure constitute a very promising class of materials. They possess a great potential as an alternative to the currently used steel grades in high temperature applications. Intermetallics-containing nanocomposites, such as those with the Fe₃Al compound being one of the phases, may open a way towards future automotive and energy-conversion technologies with lower fuel consumption and reduced environmental impact. We employ quantum-mechanical calculations to analyze relations between ordering tendencies of Al atoms in the disordered Fe-18.75at.%Al phase on one hand and thermodynamic, structural and magnetic properties of Fe-Al-based nanocomposites on the other. When comparing supercells modeling disordered Fe-Al phase with different atomic distribution of atoms we find out that the supercell without 1st and 2nd nearest neighbor Al-Al pairs has a lower energy than that mimicking a perfect disorder (a special quasi-random structure, SQS). Further, coherent interfaces with (001), (110) and (1-10) crystallographic orientations between Fe₃Al compound and SQS Fe-Al phase have higher energies than those exhibiting atomic distribution without 1st and 2nd nearest neighbor Al-Al pairs.

Keywords: Nanocomposites, Fe-Al based superalloys, ab initio calculations, interface energies

1. INTRODUCTION

The development of new lightweight metallic materials is critically important for many energy-conversion units and automotive and aerospace applications. Low-cost low-density materials operating at higher temperatures would mean lower fuel consumption or environmentally cleaner and more efficiently produced electricity. To invent new strategies in materials design of these advanced materials, a thorough understanding of fundamental mechanisms in existing lightweight alloys has to be achieved. Two basic options in materials optimization are their chemical composition and structure. Both characteristics are mutually interlinked and inherently multi-scale in their nature what makes them challenging to study. We address these fundamental aspects for an important class of lightweight materials, iron-rich Fe-Al alloys. Iron aluminides represent a very promising class of intermetallics with a great potential for substituting stainless steels at elevated and high temperatures. Noteworthy is their excellent chemical resistance to corrosion and sulfidation processes [1], low cost of their constituents, high strength, and particularly their density (5700-6700kg/m³), lower than that of steel. Unfortunately, a wider use of Fe-Al-based materials is partly hampered by their moderate ductility at ambient temperatures and low strength at elevated temperatures.

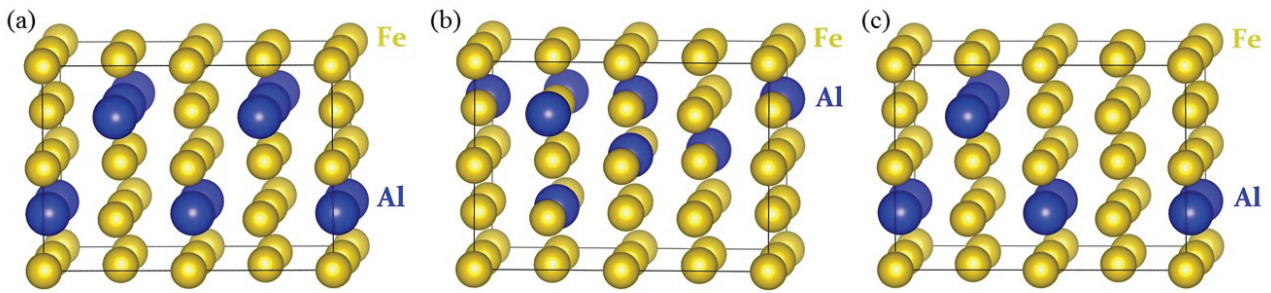


Figure 1 Schematic visualization of 32-atom $\sqrt{2} \times \sqrt{2} \times 1$ (times 16 atoms) supercells used in our *ab initio* calculations: (a) the ordered intermetallic compound Fe_3Al with the supercell stoichiometry $\text{Fe}_{24}\text{Al}_8$, (b) special quasi-random structure (SQS) as a model for a perfectly disordered phase with the supercell stoichiometry $\text{Fe}_{26}\text{Al}_6$ and (c) a disordered supercell without any 1st and 2nd nearest neighbor Al-Al pairs

Consequently, current materials-design activities are focused on obtaining a comprehensive understanding of the dependence of materials properties on the structure and composition. We employ quantum-mechanical calculations to address relations between thermodynamic, structural and magnetic properties of a disordered Fe-18.75at.%Al phase on one hand and different distributions of Al atoms in this phase on the other. Subsequently, we also analyze the impact of different atomic distributions on the interface energies when the Fe-18.75at.%Al phase coherently co-exists with the Fe_3Al intermetallics.

2. COMPUTATIONAL METHODOLOGY

Our first-principles calculations were performed within the framework of density functional theory [2, 3] using the Vienna Ab initio Simulation Package (VASP) [4, 5] and projector augmented wave pseudopotentials [6, 7]. The exchange and correlation energy was treated in the generalized gradient approximation as parametrized by Perdew and Wang [8] using the Vosko-Wilk-Nusair correction [9]. We used a plane-wave energy cut-off of 350 eV and a $6 \times 6 \times 10$ Monkhorst-Pack k-point mesh in the case of 32-atom $\sqrt{2} \times \sqrt{2} \times 1$ (times 16 atoms) supercells for calculations of properties of individual phases (see **Figure 1**).

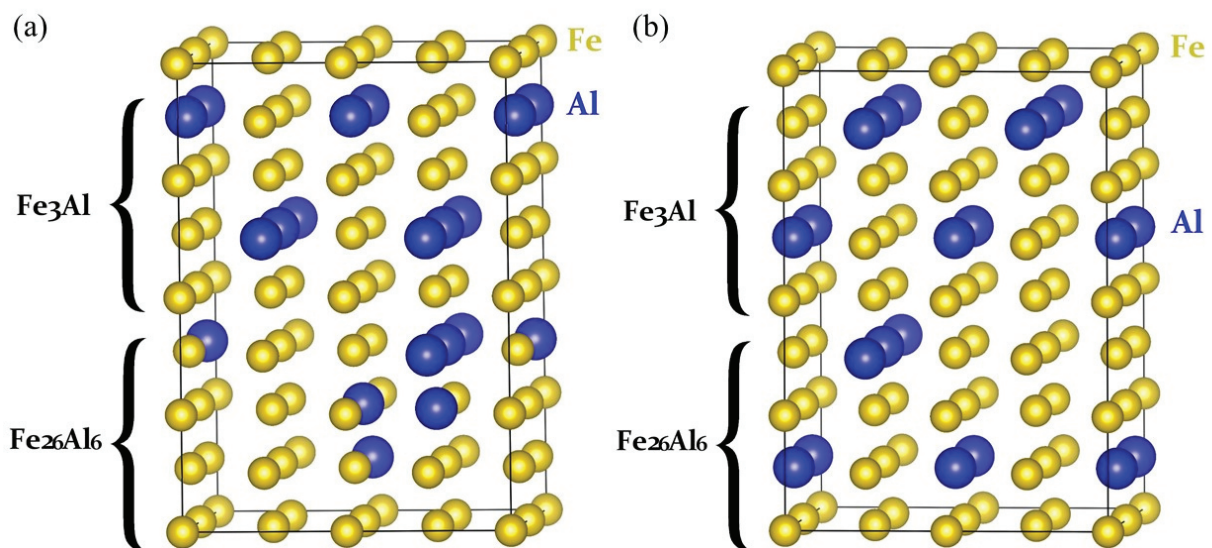


Figure 2 Visualization of supercells used to model (001) interfaces between the ordered Fe_3Al compound on one hand and the Fe-18.75at.%Al phase described by (a) a fully disordered distribution of Al atom in an iron matrix (a special quasi-random structure, SQS) or (b) a distribution of Al atoms without any 1st and 2nd nearest neighbor Al-Al pairs

We have used a 32-atom supercell for the Fe₃Al compound (a supercell in **Figure 1a** has the stoichiometry Fe₂₄Al₈) as well as for the disordered Fe-18.75at.%Al phase. In the latter case we have used two different supercells (**Figure 1b, c**) with the stoichiometry Fe₂₆Al₆ with different internal distribution of atoms. One supercell (**Figure 1b**) has the atoms distributed according to a special quasi-random structure (SQS) concept [10] and we obtained it from the USPEX code [11-13]. Another supercell has a distribution of Al atoms without any 1st and 2nd nearest neighbor Al-Al pairs (**Figure 1c**). When modeling interfaces, we have employed 64-atom supercells which are shown in **Figure 2** for the (001) interface and in **Figure 3** for the (110) and (1-10) interfaces. The corresponding k-point meshes were 6x6x5 in the case of supercells with the (001) interfaces and 6x3x10 in the case of (110) and (1-10) interfaces. The formation of a phase with m atoms of Fe and n atoms of Al was computed from the energy of this phase $E(\text{Fe}_m\text{Al}_n) - m^*\mu^{\text{Fe}} - n^*\mu^{\text{Al}}/(m+n)$ where μ^{Fe} and μ^{Al} are chemical potentials of ferromagnetic bcc Fe and non-magnetic fcc Al, respectively.

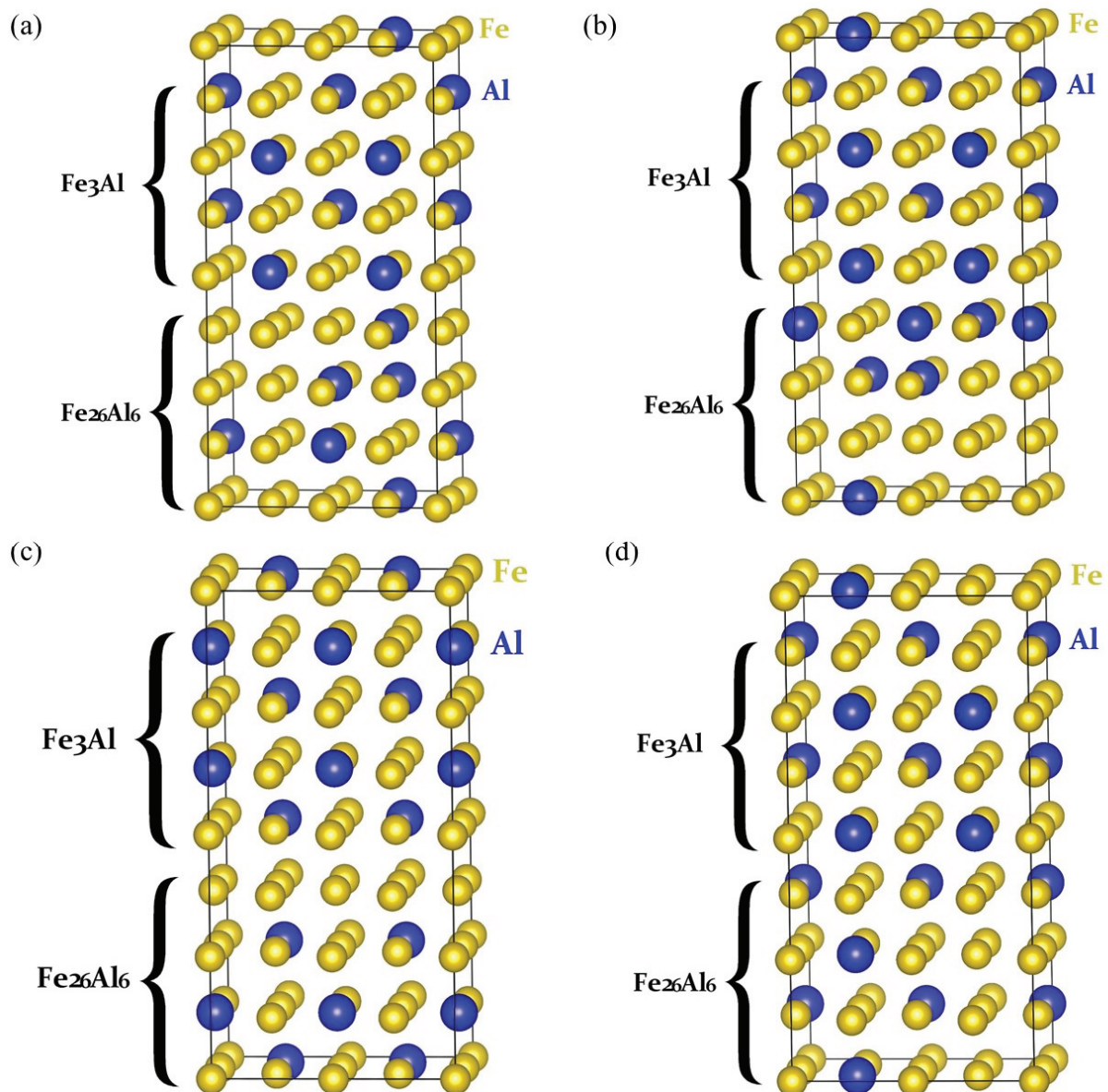


Figure 3 Visualization of supercells used to model interfaces between the ordered Fe₃Al compound and the Fe-18.75at.%Al phase described either by a fully disordered SQS distribution of Al atoms in an iron matrix (a,b) or by a distribution of Al atoms without any 1st and 2nd nearest neighbor Al-Al pairs (c,d) in the case of (110) interfaces (a,c) and (1-10) interfaces (b,d)

Table 1 Quantum-mechanically calculated formation energies (in eV/atom), equilibrium atomic volumes (in Å³/atom) and total magnetic moments per 32-atom supercell as obtained for the compound Fe₃Al and two models for disordered Fe-18.75at.%Al phase - either with a fully disordered special quasi-random structure (SQS) or with a partly ordered distribution of Al atoms when there are no 1st and 2nd nearest neighbor Al-Al pairs. Selected results are compared with *ab initio* calculations from Ref. [14] (where a little bit different computational set-up was used).

Properties of 32-atom supercells	compound Fe ₃ Al	Fe-18.75at.%Al SQS	Fe-18.75at.%Al no 1 st & 2 nd Al-Al
Formation energy (eV/atom)	-0.194 (-0.202 [14])	-0.119	-0.144
Atomic volume (Å ³ per atom)	11.78 (11.82 [14])	11.84	11.76
Magnetic moment (μ _B per 32 atoms)	47.51	56.57	55.49

3. RESULTS

Table 1 summarizes formation energies, equilibrium volumes per atom as well as total magnetic moments of both Fe₃Al compound and two supercells modeling Fe-18.75at.%Al phase. Regarding the Fe₃Al, our current results are in excellent agreement with those previously published in Ref. [14] despite of the fact that a different set of pseudopotentials and different parametrization of the exchange-correlation functional was used there. As far as the Fe-18.75at.%Al phase is concerned, the formation energy of the supercell with no 1st and 2nd nearest neighbor Al-Al pairs is clearly lower than that of the SQS supercell and, therefore, the former is predicted to represent the equilibrium structure. This lower-energy distribution of atoms has also a little bit lower total magnetic moment (55.49 μ_B per 32 atoms) than the SQS structure (56.57 μ_B per 32 atoms). Employing a magneto-volumetric argument, which was successfully used to explain a lattice parameter composition anomaly in Fe-Al alloys in Ref. [14], we can then also understand why the equilibrium volume per atom is lower in the phase with the lower total magnetic moment, i.e., the lower the magnetic moment, the lower the volume. This lower volume in the case of the lower-energy atomic distribution is critically important for the existence of a superalloy microstructure in which both phases (Fe₃Al and Fe-18.75at.%Al) coherently co-exist because a too big lattice parameter mismatch between them would not allow for a coherency. Regarding the Fe₃Al compound and the Fe-18.75at.%Al phase modeled by a distribution without any 1st and 2nd nearest neighbor Al-Al pairs, the equilibrium atomic volumes are nearly identical, 11.78 and 11.76 Å³ per atom, respectively.

Table 2 contains our *ab initio* calculated interface energies between Fe₃Al compound and our two models for the disordered α-phase Fe-18.75at.%Al - either the SQS or partly ordered distribution of Al atoms when there are no 1st and 2nd nearest neighbor Al-Al pairs. In general, the interface energy of a composite consisting of phases “phase-1” and “phase-2” is computed from the energy of the studied composite $E(\text{phase-1}/\text{phase-2})$ lowered by energies of the two individual phases $E(\text{phase-1})$ and $E(\text{phase-2})$ and this difference is divided by twice the interface area A , i.e. $[E(\text{phase-1}/\text{phase-2}) - E(\text{phase-1}) - E(\text{phase-2})]/2 \cdot A$, where the interface area is included twice because there are two interfaces per computational composite supercell (due to the periodic boundary conditions). The interface energies for the nanocomposites formed by Fe₃Al and Fe-18.75at.%Al phase with the SQS model for the α-phase are very low and very similar for different crystallographic orientations of interfaces. Therefore, if this scenario occurs in reality, it is unlikely that any well-shaped inhomogeneities (e.g., cuboids) would form because there is very little thermodynamic preference for any of the studied interface orientations.

The interfaces energies between Fe₃Al and the Fe-18.75at.%Al α-phase modeled by a supercell without any 1st & 2nd nearest neighbor Al-Al pairs turned out to be very small and negative for all three crystallographic orientations of the interface. This seemingly unexpected result can be explained as follows.

Table 2 *Ab initio* computed interface energies between Fe₃Al compound and our two models for disordered α -phase Fe-18.75at.%Al - either a fully disordered special quasi-random structure (SQS) or a partly ordered distribution of Al atoms when there are no 1st and 2nd nearest neighbor Al-Al pairs.

Interface energies (J/m ²)	(110)	(1-10)	(001)
Fe ₃ Al/Fe-18.75at.%Al - SQS full disorder	0.020	0.022	0.019
Fe ₃ Al/Fe-18.75at.%Al - no 1 st & 2 nd Al-Al	-0.005	-0.004	-0.004

First, our model for the α -phase without any 1st & 2nd nearest neighbor Al-Al pairs can be considered as a particular form of Fe₃Al with two point defects, i.e. two Al atoms replaced by Fe atoms (compare **Figure 1a** and **Figure 1c**). It should be also mentioned that the energy gain per atom in the calculated types of nanocomposites (visualized in **Figures 2 and 3**) compared with the energy of independent phases (**Figure 1**) is extremely low, only about 0.0004 - 0.0005 eV per atom, and this value is, in fact, lower than the error bar of our calculations. Thermodynamically, the fact that the formation of interfaces does not cost nearly any energy when the phase neighboring Fe₃Al is just point-defected Fe₃Al itself is also perfectly in line with a very broad homogeneity range of Fe₃Al (see the Fe-Al phase diagram, e.g., in Ref. [14]). This type of nanocomposite could be probably considered as a one-phase material, i.e. Fe₃Al compound with quite a high number of point defects.

4. CONCLUSIONS

We have used *ab initio* calculations to test a possibility of formation of a superalloy-type of nanocomposite microstructure in the case of Fe-Al where the ordered intermetallics Fe₃Al with the D0₃ structure coherently co-exists with a disordered solid solution of Al in Fe (the α -phase) with the composition Fe-18.75at.%Al. In order to examine the impact of different distributions of Al atoms in the α -phase on the thermodynamic, structural and magnetic properties of both the α -phase and the nanocomposites, we have employed two different types of distribution of Al atoms, a special quasi-random structure (SQS) mimicking a perfect disorder and a distribution without any 1st and 2nd nearest neighbor Al-Al pairs. All individual phases were modeled by 32-atom supercells and the nanocomposites were just equal-molar-amount combination of these stacked in different crystallographic directions. The α -phase distribution without the 1st and 2nd nearest neighbor Al-Al pairs is found to have a lower formation energy than the SQS, and is thus thermodynamically preferred to occur if conditions permit, and it has also by 1.9 % lower volume and by 0.68 % total lower magnetic moment than the SQS phase.

Regarding the nanocomposites, those combining Fe₃Al compound with the SQS α -phase have very low interface energies (0.019 - 0.022 J/m²) which are very similar for all three studied crystallographic orientations of the interface, (110), (1-10), (001). The nanocomposites with the α -phase distribution without the 1st and 2nd nearest Al-Al pairs exhibit the interface energies lower than in the case of the SQS distribution of atoms in the α -phase. They reach even negative values, from -0.004 to -0.005 J/m². The reason for this is two-fold. First, the distribution of Al atoms without 1st and 2nd nearest neighbor Al-Al pairs is, in fact, the same as in the Fe₃Al ordered compound and our model for the α -phase could be considered as Fe₃Al with a few point defects. Considering a very wide homogeneity range of Fe₃Al, our composites can be considered as alternation of perfect and point-defected Fe₃Al. Second fact to be taken into account is the actual energy gain to form the studied nanocomposites with the negative interfaces energies which is extremely low, only 0.0005 eV/atom what is, in fact, lower than the error bar of our calculations.

In future, we would like to extend our study to elastic properties of the above discussed nanocomposites and compare them with the elasticity of individual phases (see, e.g. Ref. [15]) as well as predict changes in thermodynamic properties of these nanocomposites due to the existence of internal interfaces separating the phases (see the impact of grain boundaries on the melting temperature in Ref. [16]).

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