Calculation of Interfacial energies for θ' percipitates in Al-Cu matrix

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Abstract

We present a study to model the interface energies of precipitates growing in a mtrix. We implement DFT techniques to calculate the bulk energies of Al-Cu matrix, θ' precipitates , inerface energicies of the matrix and θ' precipitates and the energy due to the coherency strain E_{cs} associated with the interface. We try to calculate all the parameters that are required by models like phase field methods to understand the microstructure evolution thus enabling a multiscale approach to solve engineering problems.

Keywords: DFT, Al-Cu, θ' Precipitates, interface energies, coherency strain

1. Introduction

Al-Cu alloy is a widely used alloy whose practical usage ranges from aerospace to automotive industries. This is primarily because of its high strength to weight ratio. Due to its technological importance this binary system is well studied and the theories developed to explain its precipitation hardening forms the basis of most of age-hardenable alloy[1]. Though θ is thermodynamically the most stable phase, the formation of θ phase is not kinetically favoured at small sizes. Hence the precipitation starts off with meta stable phases and later converts to θ. The precipitation sequence observed is as follows.

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$$\text{GP1} \rightarrow \theta'' \rightarrow \theta' \rightarrow \theta[2].$$

It has been noted that the maximum strength of the alloy is attained when θ' exists. Further, it is also observed that the morphology,shape and size of the θ' precipitates also influence the strength of the alloy to a great extent.

Phase field models have been developed that can predict the growth of the θ' precipitates. KhachaturyanHairapetyan is one such framework which seems to reproduce various morphologies obtained from experiments [3]. However, these models depend upon parameters like interfacial energy and many other thermoelastic properties which are quite hard to measure experimentally.

Hence, we will try to calculate properties like interface energy using DFT. The properties we are intending to calculate from DFT include, Bulk energies of Al-Cu, Bulk energies of θ' and the interfacial energy corresponding to different interfaces. This data would enable us to implement KhachaturyanHairapetyan model to understand the growth of the θ' precipitates[4]. Once we are able to predict the morphology of θ' precipitates for various process parameters we would be in a position to calculate its mechanical properties.

2. Creation of Supercell

The first step in calculation of the interfacial energy is the generation of supercell. It has been experimentally shown, through numerous TEM, studies that orientations relations exist between θ' precipitates and the Al-Cu matrix and it is given by $(100)_{\theta'}||\{001\}_{Al}$[5].Hence, we will be performing calculations in supercells with the orientation relationship satisfied. The creation of the supercell is a two step process. First, the supercell of Al-Cu matrix has to be generated. Then the Al_2Cu precipitate must be added at an end subjected to the orientation relationship.

2.1. Generation of Al-Cu Matrix

Al-Cu matrix is a dis-ordered system in a FCC lattice. To generate a dis-ordered supercell with maximum randomness *mcsqs* code developed as a part

of $ATAT$ is used[6]. The supercell has been generated with 32 atoms. The supercell has been generated with its unit cell vectors parallel to the 3 cartesian co-ordinates so that the generation of the supercell with the interface becomes much easier. The generated supercell is as shown in Fig 2a .

2.2. Generation of θ' precipitate

θ' precipitate has a Body- centered Tetragonal structure. The structure of $Al_2Cu(\theta')$ precipitate is as shown in Fig 1 .

2.3. Generation of Supercell with the interface

With the structures of Al-Cu matrix and θ' precipitate available. We can manually create a supercell with the orientation relationship discussed above. The final supercell that can be used for DFT calculations is depicted in Fig 4. The interface has also been marked for visualization purpose.

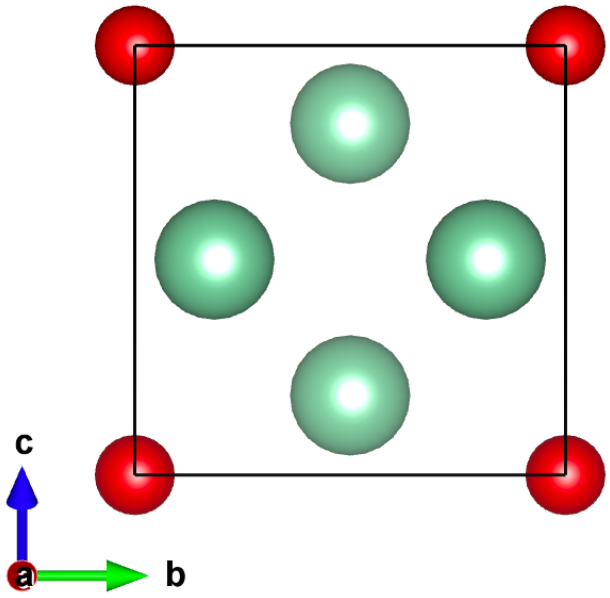
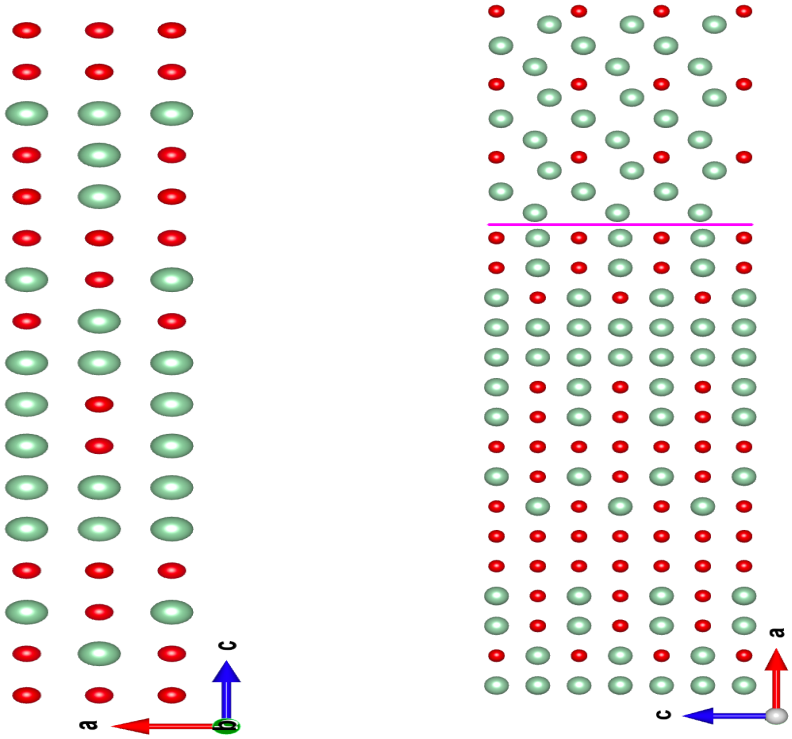


Figure 1: Primitive unit cell of θ' precipitate



(a) Dis-ordered Al-Cu matrix

(b) Supercell used for calculation of interfacial energiy

Figure 2: Supercells used as input for DFT calculations

3. Calculation of Energies

3.1. Bulk Energies

The bulk energies of the Al-Cu matrix and the Al_2Cu precipitates can be calculated by using Quantum Espresso. The values obtained from the code would be at $T = 0K$. To calculate the energies at a higher temperature we can use the first principle MSCE Hamiltonian. We can calculate the energy of the Al-Cu (E_{ss}) for various compositions and temperatures using Monte-Carlo simulations. The difference between (E_{ss}) and the enrgy of the constituent

atoms gives the enthalpy of mixing.

$$\Delta H_{ss} = E_{ss} - [X_{Cu}E_{Cu} + X_{Al}E_{Al}] \tag{1}$$

Thus, with 1 we can calculate the enthalpy of mixing as a function of temperature and composition. To calculate the configurational entropy we use equation 2[7].

$$\Delta S_{config} = \Delta S_{ideal} + \frac{\Delta H_{ss}}{T} - k_b \int_0^{\beta} \Delta H_{ss}(\beta')d\beta' \tag{2}$$

Once, we calculate the enthalpy of mixing and configurational entropy as a function of temperature we can calculate the free energy by equation 3.

$$\Delta F_{ss} = \frac{1}{\beta} \int_0^{\beta} \Delta H_{ss}(\beta')d\beta' - T\Delta S_{ideal} \tag{3}$$

3.2. Interfacial and Coherent Energy

After calculating the bulk energies of the system we can calculate the interfacial energy. However, the difference in the energy between and the energy of a supercell with Al-Cu matrix and θ' precipitate and its constituent atoms can not be equated to the intefacial energy as it has a significant amount of strain energy E_{cs} associated with it as it is a coherent interface. To calculate the energy of the interface equation 4 is used[8].

$$\delta E_{sl}(N, \hat{G}) = \frac{2\sigma(\hat{G})A}{N} + \delta E_{cs}(\hat{G}) \tag{4}$$

where,

N is the number of atoms in the supercell,

δE_{sl} is the increase in energy due to the interface,

δE_{cs} is the energy due to the coherent strain.

Thus by plotting δE_{sl} as a function of $\frac{1}{N}$ we can calculate the interfacial energy from the slope and the E_{cs} from the intercept.

4. Results and Discussion

We have been able to create a supercell which would enable us to calculate the interface energies of the precipitate and the matrix. Further, we have also proposed a methodology to calculate the interfacial energy and E_{cs} which would enable us to predict the microstructure evolution during aging more accurately using techniques like phase field methods.

5. Future Work

To take this study further, we would like to incorporate vibration entropy in equation 3. This would significantly increase the complication of the problem but the effect of vibrational entropy on the energies would be interesting to look at. Further, we can extend this model to other alloy systems as well to understand their growth kinetics as well. We can also create supercells by substituting few atoms from the interface with atoms like Si to understand the effect of such atoms on the kinetics of growth. Since our aim is to restrict the growth of the precipitates we can find out what elements reduce the interfacial energy and make it stable.

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