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Full length article

Solute segregation at the Al/θ'-Al_2Cu interface in Al-Cu alloys☆

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ABSTRACT

A recent investigation has confirmed that solute atoms segregated to the interfaces between aluminum and θ'-Al_2Cu can extend the stability of metastable θ' to higher temperatures. Herein, we present an extensive first-principles database of the segregation energies of 34 elements to the Al/θ' interface and identify key descriptors that can guide the design of higher temperature Al-Cu alloys. We find that the segregation energies are strongly correlated with the size and volume of solute atoms and their solubilities within θ'. We provide a physical/chemical basis to the experimentally observed elemental hierarchy in terms of the ability of individual elements to stabilize the Al/θ' interface. Finally, we suggest a new microalloying strategy that offers opportunities to further increase the critical temperature limit of Al-Cu alloys.

1. Introduction

The use of cast aluminum alloys to replace cast iron counterparts in passenger vehicle powertrains is critical to reducing vehicle weight. For example, several cast Al alloys (206, 319, 356, and A356) have been used to fabricate automotive engine components, such as cylinder heads, over the past a couple decades. A recent trend in the design of modern automotive powertrains is pursuing higher efficiency designs through smaller, turbocharged engines. These boosted engines also lead to an increase in the operating temperature of the engine, particularly the cylinder head. Among the Al alloys currently used in the automotive industry, those based on Al-Cu-(Si) (e.g., 319) offer improved elevated temperature mechanical properties compared to those based on Al-Si (e.g., 356 and A356) because of the formation of θ'-Al_2Cu, which is thermodynamically metastable in nature. As the temperature increases, the θ' rapidly coarsens; and at ~250°, it transforms to θ-Al_2Cu, which is thermodynamically stable, but incoherent with the Al matrix [1,2]. The formation of the θ phase leads to decreasing mechanical properties. Hence, increasing the stability of the metastable θ' phase to higher temperatures has been regarded as a grand challenge in Al alloy design.

Recently, Shyam et al. [3] have experimentally demonstrated that the operating temperature of cast Al-Cu alloys could be extended to at least 300 °C via microalloying with Mn and Zr. The mechanism behind this observation was identified as the stabilization of the strengthening θ'-Al_2Cu precipitate to significantly higher temperatures than previously reported. An extensive experimental investigation using scanning transmission electron microscopy (STEM) and atom probe tomography (APT) revealed that solute atoms segregated to the coherent and semi-coherent interfaces between Al and θ'-Al_2Cu contributed to the stabilization of the interfaces. If the stability of such interfaces can be systematically harnessed, the reported observation opens up opportunities to further push the elevated temperature limits of precipitation hardened alloys by extending the stability range of key intermetallics via matrix/precipitate interface engineering.

Segregation of trace or microalloyed solutes to the interface between the Al matrix and precipitate phases has been previously

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reported and extensively investigated. Examples are partitioning and segregation of Si [4], Ag [5], Sn [6], and Sc [7–9] within θ'-Al_2Cu and to the Al/θ' interface, and the segregation of Cu to the Al/Q′ interface in the Al-Mg-Si-Cu alloy [10]. It has been proposed that segregation of the solute atoms lowered the interfacial energy and limited the coarsening of the precipitates.

Shyam et al. [3] also have shown that a hierarchy and synergy exist in terms of the ability of individual or a combination of elements to stabilize the key interfaces in θ' precipitates at high-temperatures. They have demonstrated that either Mn or Zr additions alone provide stabilization of θ' to a certain extent, but the critical temperature where strength is preserved can be further extended by adding both Mn and Zr. However, the underlying principle behind the observed elemental hierarchy and synergy, which would be extremely useful for high-temperature alloy design, is currently unknown. Despite the importance of understanding the segregation behavior of various solutes segregating to the interfaces (i.e., coherent and semi-coherent) between Al/θ', a comprehensive understanding of the mechanism of solute segregation to these interfaces does not exist.

Herein, we present an extensive first-principles database of the solute segregation energies of 34 elements segregating to the Al/θ' interfaces based on a density functional theory (DFT) approach. The current DFT segregation energy database of isolated solutes can serve as a reference for multiple solute segregation calculations in the future. We provide correlation analyses between the DFT solute segregation energies and atomistic descriptors to elucidate the key descriptors that govern the stabilization of θ' at high temperatures. The knowledgebase generated in the present work will support the accelerated design of high-temperature alloys by providing a physical/chemical basis of elemental hierarchy in stabilizing key intermetallics in precipitation hardened alloys via interface engineering.

2. Computational method

2.1. Supercell approach

2.1.1. Interfaces between the Al matrix and θ'-Al_2Cu precipitate

We used a defect supercell approach to represent coherent and semi-coherent interfaces between Al and θ'-Al_2Cu after Biswas et al. [4]. We considered the segregation of 34 elements at both coherent and semi-coherent interfaces using 108- and 168-atom supercells, respectively, and the supercell models are presented in Fig. 1. Only one solute was introduced in each supercell, and a solute was progressively moved from the bulk toward the sharp interface to derive the solute segregation energy as a function of the distance from the interface. We considered all the crystallographically distinctive lattice sites at each platelet. As shown in Fig. 1, four platelets were used to represent the Al matrix at both interfaces. They are denoted as Al_x, where x represents the location of solutes: i the interface, and i-1 and i-2 the first and second platelets away from the interface on the matrix side. The $Al_{i\text{-}3}$ platelet was assumed to be sufficiently far away from the interface to be considered as 'bulk' and was denoted Al_b.

The solute segregation energy can be described by comparing the total energiess as shown in Eq. (1):

$$\Delta E_{seg} = E(Al_x) - E(Al_b), \tag{1}$$

where E represents the total energy obtained from first-principles DFT supercell calculations. A sharp interface model within the context of DFT is appropriate to simulate the interface between Al and θ'-Al_2Cu to investigate solute segregation, as the current work assumes a high-temperature environment, as discussed by Bourgeois et al. [11].

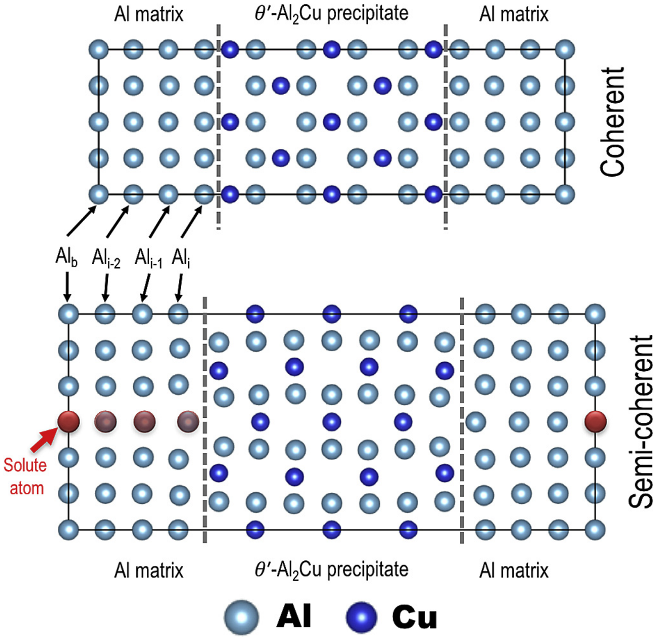

Figure 1. Supercell models used in the present DFT calculations after Biswas et al. [4] for coherent (top) and semi-coherent (bottom) interfaces between the Al matrix and θ'-Al_2Cu precipitate. The location of solute atoms in the Al matrix is represented as Alx, where x = i represents the interface platelet, x = b the bulk, and i-1 and i-2 the platelets in between. Only one solute atom was introduced in each platelet. All crystallographically distinctive positions in each platelet were considered, and the one with lowest total energy was accepted to derive the segregation energy in comparison with the total energy at the bulk location as shown in Eq. (1).

2.1.2. Special quasirandom structures (SQSs)

Biswas et al. [4] have investigated the segregation of solutes within θ'-Al_2Cu by deriving the chemical potential of Cu with respect to θ'. We deem the segregation of solutes within a precipitate as partitioning. Thus, we qualitatively consider the solubility of individual solute elements in the Al and Cu sublattices within θ' via special quasirandom structures (SQSs) [12] that can mimic random mixing between solute atoms and the respective Al/Cu sublattices. SQSs can serve as structural templates to derive the mixing energies within the context of DFT total energy calculations, and they have been successfully employed in a number of alloy systems [13–16].

We generated two 48-atom SQSs, $(Al,X)_2Cu$ and $Al_2(Cu,X)$, at equimolar compositions that assume a regular solution. The generated SQSs could successfully satisfy correlation functions of pair clusters up to 7th-nearest neighbors and perfect triplet matches on both SQSs. The hypothetical end-members to derive the mixing energies, i.e., X_2Cu and Al_2X in the θ'-Al_2Cu structure, also were calculated from DFT.

2.2. First-principles calculations

We used the Vienna Ab initio Simulation Package (VASP) [17,18] for the DFT calculations. All the DFT supercell and SQS calculations were performed using the projector augmented wave [19] potentials and the generalized gradient approximation [20]. We used Perdew-Burke-Ernzerhof for the exchange–correlation functional [21]. Because of the large number of interface supercell calculations required to generate the DFT solute segregation energy database, we used the efficient graphics processing unit (GPU) version of