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Stress/strain aging mechanisms in Al alloys from first principles

Kang LUO[1], Bing ZANG[1], Shang FU[1], Yong JIANG[1, 2], Dan-qing YI[1, 2]

1. School of Materials Science and Engineering, Central South University, Changsha 410083, China;
2. Key Lab of Nonferrous Materials of Ministry of Education, Central South University, Changsha 410083, China

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Abstract: First-principles based calculations were carried out to explore the possible mechanisms of stress/strain aging in Al alloys. Potential effects of temperature and external stress/strain were evaluated on the solvus boundary of Al_3Sc in Al−Sc alloy, and the interface energy of Al/θ'' in Al−Cu alloys. Results show that applying tensile strain/stress during conventional aging can significantly decrease the solubility entropy, by red-shifting the phonon DOS at high states. The resulted solvus boundary would shift up on the phase diagram, suggesting a reduced solubility limit and an increased maximum possible precipitation volume of Al_3Sc in Al−Sc alloy. Moreover, the applied strain/stress has different impacts on the formation energies of different orientated Al/θ'' interfaces in Al−Cu alloys, which can be further exaggerated by the Poisson effect, and eventually affect the preferential precipitation orientation in Al−Cu alloy. Both mechanisms are expected to play important roles during stress/strain aging.

Key words: stress aging; solubility limit; interface energy; first-principles

1 Introduction

Precipitation hardening, also called age hardening, is a most widely used heat treatment technique aimed to increase the yield strength of malleable alloys. It relies on changes in solid solubility with temperature to produce fine size second-phase precipitates, to impede the movement of dislocations or grain boundaries during plastic deformation. The yield strength of the alloy is thus largely dictated by the number density and spatial distribution of the precipitates. It has been noticed [1−3] that, applying stresses/strains during the aging process, namely stress/strain aging, can impose a great effect on the habit planes, density and size of second-phases in the alloys, and hence the effectiveness of age hardening. NAKADA and LESLIE [4] first proposed that the commensuration strain due to the lattice misfit of coherent precipitates might be largely compensated by the applied stress/strain, and thus the nucleation and perhaps the growth of the precipitates can be enhanced. Based on an interface diffusion model, other researchers [5,6] demonstrated that for Al−Cu alloys, stress/strain aging may play a more effective role in the nucleation than the growth stage. HOSFORD and AGRAWAL [7] further improved the model by considering the stress-biased diffusion of solute atoms. All these mechanism models were focused on the nucleation and growth of the precipitates. We still lack the knowledge of whether and how an external stress/strain impacts the solvus boundary, namely, whether and how the maximum possible volume fraction of the precipitate phase vary differently with temperature when subjected to stress/ strain. On the other hand, interface structure and composition of a precipitate phase are critical in determining its nucleation and growth behaviors, and as well its interaction with dislocations. Thus, interface energy under stress/strain also needs a thorough investigation.

In this work, we plan to develop a density functional theory (DFT) based strategy to investigate the impact of temperature and external stress/strain on both the solvus boundary (i.e., solubility limit) and the interface energetics of the second phase precipitates in alloys. This strategy will be demonstrated for $L1_2$−Al_3Sc in an Al−Sc alloy and the θ'' interface in an Al−Cu alloy. Based on the obtained results, the possible mechanisms of stress/strain aging in Al alloys are discussed. This approach would enable us to eventually achieve the energetics- and interface-level understanding of stress/

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Corresponding author: Yong JIANG; Tel: +86-731-88836320; Fax: +86-731-88830263; E-mail: yjiang@csu.edu.cn
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strain aging effects.

2 Calculation methods

All calculations were performed using the semi-commercial DFT code VASP [8]. The plane-wave basis sets were generated with valence configurations of Al $3s^2 3p^1$, Cu $3d^{10}4s^1$ and Sc $3p^6 4s^2 3d^1$. The electron−ion interaction was described by the projector augmented wave method within the frozen-core approximation [9]. The exchange-correlation functions used the generalized gradient approximation [10]. For hcp-Sc calculations in a 2×2×2 16-atom orthorhombic superlattice, an adequately high energy cutoff of 300 eV and a 15×15×9 Monkhorst–Pack (MP) k-mesh for Brillouin-zone integrations were used. Calculations on the precipitate phase $L1_2$-Al_3Sc used a 2×2×2 32-atom fcc superlattice and a 9×9×9 MP k-mesh. The calculations for a dilute Al−Sc solid solution ($Al_{31}Sc$) used a 2×2×2 fcc Al superlattice and a 9×9×9 MP k-mesh. The coherent Al/θ'' interface was modeled using an Al/θ''/Al sandwich configuration with an 18×18×1 MP k-mesh. All structures were fully relaxed until the total force on each ion converged to to within 0.01 eV/Å. Phonon calculations employed the direct supercell approach within the quasiharmonic approximation [11]. Force constants were calculated within the density-functional perturbation theory [12], using a stringent ionic force criterion of 10^{-7} eV/Å. The phonon modes were calculated from the force constant matrix using PHONOPY [13].

3 Results and discussion

3.1 Solvus boundary under stress/strain

The orientation relationship of $L1_2$-Al_3Sc in the matrix is {001}[001]Al_3Sc//{001} [001]Al [14]. Following the experimental practices, we apply a series of uniaxial tensile strains to the matrix (along Al[001]), to assess the maximum possible stress/strain effect on the solvus boundary of $L1_2$−Al_3Sc in Al−Sc alloys. In the isotropic elastic regime, the tensile stress along [001] inevitably leads to a compression in both the [010] and [100] directions (Poisson effect). Consequently, the cubic lattices may distort to an orthorhombic structure with $a>b=c$. The solubility, x_0, can be expressed as [15]

$$x_0(T)=\exp\left(\frac{-\Delta F^{\mathrm{sol}}}{k_{\mathrm{B}}T}\right)=\exp\left(\frac{-\Delta H^{\mathrm{sol}}}{k_{\mathrm{B}}T}\right)\times\exp\left(\frac{\Delta S^{\mathrm{sol}}_{\mathrm{vib}}}{k_{\mathrm{B}}}\right) \quad (1)$$

where k_{B} is the Boltzmann constant. The solubility enthalpy, $\Delta H^{\mathrm{sol}}=\Delta H_{\mathrm{Al_{31}Sc}}-\Delta H_{\mathrm{Al_3Sc}}$ is defined as the difference between the formation enthalpies of $Al_{31}Sc$ and $L1_2$-Al_3Sc, and

$$\Delta H=E_{\mathrm{Al}_x\mathrm{Sc}}-xE_{\mathrm{Al}}-E_{\mathrm{Sc}} \quad (2)$$

where $E_{\mathrm{Al}_x\mathrm{Sc}}$ represents the total energy of $Al_{31}Sc$ or $L1_2$−Al_3Sc, and E_{Al} (or E_{Sc}) is the elemental energy at its pure state. With Eq. (2), the solubility enthalpy, ΔH^{sol}, can be rewritten as

$$\begin{aligned}\Delta H^{\mathrm{sol}}&=\Delta H_{\mathrm{Al_{31}Sc}}-\Delta H_{\mathrm{Al_3Sc}}\\&=(E_{\mathrm{Al_{31}Sc}}-31E_{\mathrm{Al}}-E_{\mathrm{Sc}})-(E_{\mathrm{Al_3Sc}}-3E_{\mathrm{Al}}-E_{\mathrm{Sc}})\\&=E_{\mathrm{Al_{31}Sc}}-E_{\mathrm{Al_3Sc}}-28E_{\mathrm{Al}}\end{aligned} \quad (3)$$

and similarly,

$$\Delta S^{\mathrm{sol}}=S_{\mathrm{Al_{31}Sc}}-S_{\mathrm{Al_3Sc}}-28S_{\mathrm{Al}} \quad (4)$$

The vibrational entropies can be further evaluated from the obtained phonon DOS as

$$S=k_{\mathrm{B}}T\int_0^{\infty}\ln\left[2\sinh\left(\frac{h\nu}{2k_{\mathrm{B}}T}\right)\right]g(\nu)\mathrm{d}\nu \quad (5)$$

where h is Planck's constant, υ is the frequency, and $g(\upsilon)$ is the phonon DOS.

Table 1 compares the calculated elastic properties of Al, the dilute solid solution $Al_{31}Sc$, and the compound $L1_2$−Al_3Sc. Note that the elastic properties of Al and $Al_{31}Sc$ are quite close. $L1_2$−Al_3Sc has much higher shear and elastic modulus, and a very low Poisson ratio. Note, the elastic modulus of $L1_2$−Al_3Sc is about three times higher than that of Al or $Al_{31}Sc$, and thus, upon the same tensile stress, the stretching of $L1_2$−Al_3Sc should be about one third of the matrix.

Table 1 Calculated bulk elastic properties

Item	C11/ GPa	C12/ GPa	C44/ GPa	*B*/ GPa	*G*/ GPa	*E*/ GPa	ν
Al	97	62	21	74	20	54	0.38
$Al_{31}Sc$	103	58	23	73	21	62	0.36
Al_3Sc	180	37	69	85	70	165	0.18

Vibration calculations are then performed on all the distorted (orthorhombic) structures. Here, we only consider the strains below 1%, to ensure the matrix to maintmain elastity. For the reason mentioned above, only one third of the applied strains will be imposed on $L1_2$−Al_3Sc. Also, according to Eqs. (3) and (4), Sc does not really contribute to solubility enthalpy and entropy, and hence will be ignored in such calculations. The computed solubility enthalpies are listed in Table 2. Note that ΔH^{sol} does not change obviously with the strains, and thus strain effect on phonon vibrations can be important. Figure 1 compares the calculated phonon DOS under strains for the three systems. A left-shift is evident in both of the two high states, particularly for Al and Al_3Sc.