The structural stabilities of $Al_3(Sc_{1-x}M_x)$ by first-principles calculations

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ABSTRACT

The positive effects of Al_3Sc phase on Al–Sc alloys can be promoted by adding to the third elements. The structure properties of Al_3Sc when it dissolves the third elements are investigated by first-principles calculations. Special quasirandom structures are developed for the quasi-binary $L1_2$ structures. The calculations indicate that the elements of Ti, Zr, Y and Ta tend to substitute for Sc in Al_3Sc, while Ni and Si prefer to substitute for Al. The present lattice parameters generally follow the Vegard's law. The high solubility of Ti and Y in Al_3Sc is revealed in the calculated quasi-binary phase diagram.

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1. Introduction

Al-rich Al–Sc alloys are generally used as high-strength materials. The effects of Sc addition in Al alloys are mainly attributed to the formation of Al_3Sc with cubic $L1_2$ structure, as precipitation strengthener, grain refiner, recrystallization inhibitor [1]. The elements near Sc in the period table (Y, Ti, Zr, V, Nb, and Ta etc.) are most widely used to be added to Al–Sc alloys, which can lead to the improvements of the mechanical properties, corrosion resistance and creep properties [2–6]. In addition, partial substitution of Sc by other elements can increase the ductility of Al_3Sc and decrease the cost of the alloy. The addition of Zr can further inhibit recrystallization and decrease the coarsening rate of the precipitates of Al_3Sc [7–13].

In order to understand the effect of Al_3Sc precipitation in Al–Sc alloys, it is necessary to gain more knowledge about the Al_3Sc phase. The structure and thermodynamic properties of Al_3Sc have been studied [14,15]. However, the structural properties of Al_3Sc when it dissolves the third elements have seldom been investigated by any theoretical studies. No studies have systematically clarified whether the added elements tend to substitute Sc or Al in Al_3Sc. Besides, structural stabilities of $Al_3(Sc_{1-x}M_x)$ are not clear yet.

In this paper we study the site preference of the added elements in Al_3Sc and the structural stabilities of $Al_3(Sc_{1-x}M_x)$ by first-principles calculations. As one type of the site is occupied by two kinds of atoms randomly, it conventionally needs very large supercells to represent these random structures. Thanks to the special quasirandom structures(SQSs) method proposed by Zunger et al. [16,17],

the random alloys can be directed modeled by the specially designed small periodic structures.

2. Methodologies

2.1. Generation of SQSs

The basic theories and detailed descriptions of the procedures for constructing the SQSs can be easily found in many previous literatures [16–21]. For a binary $(A_{1-x}B_x)$ substitution alloy, the correlation functions are described as $\bar{\Pi}_{k,m}$, where $k = 2, 3...,$ represent the pair, triple correlation functions, etc., and $m = 1, 2, 3...,$ represent the first, second and third-nearest distance, etc. Firstly, the correlation functions of the random alloys are calculated according to the compositions. The correlation functions of an ideal $A_{1-x}B_x$ alloy are $\bar{\Pi}_{k,m} = (2x-1)^k$. Secondly, a serial SQSs-N are calculated according to the given criterion $(\bar{\Pi}_{k,m})_{SQS} = (\bar{\Pi}_{k,m})_{Random}$ Finally, the structure is selected with the smallest correlation functions error, which is estimated by $\sum_{(k,m)}[\bar{\Pi}_{k,m} - (2x-1)^k]^2$.

SQSs were developed for quasi-binary $L1_2$ structures $A_3(B_{1-x}C_x)$ at $x = 1/2$ and $1/3$, and $(A_{1-x}B_x)_3C$ at $x = 1/6$ by using the *gensqs* code in the Alloy-Theoretic Automated Toolkit(ATAT) [22]. Including the common atoms, a total of $4N$ and $4N/3$ atoms exist in SQS-N for $A_3(B_{1-x}C_x)$ and $(A_{1-x}B_x)_3C$, respectively. For $A_3(B_{1-x}C_x)$ at $x = 1/2$ and $1/3$, we search the SQS-N whose pair correlation functions are identical to those of the random alloy up to the second-nearest neighbor pairs. The correlation functions and the pictures of the ideal and unrelaxed SQSs are shown in Table 1 and Fig. 1. A rhombohedral structure (space group R-3 m NO. 166) was obtained at $x = 1/2$ for $N = 4$. However, a total of 8 SQSs were generated at $x = 1/2$ for $N = 8$. One of the structures was selected with the

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Table 1
The correlation functions of the SQSs structures, compared with the ideal random solutions.

	$A_3(B_{1/2}C_{1/2})$				$A_3(B_{1/3}C_{2/3})$			$(A_{5/6}B_{1/6})_3C$	
	Random	SQS-4 16 atoms	SQS-8 32 atoms	SQS-8-cubic 32 atoms	Random	SQS-6 24 atoms		Random	SQS-18 24 atoms
$\bar\Pi_{2,1}$ [3]	0	0	0	0	0.11111	0.11111	$\bar\Pi_{2,1}$ [12]	0.44444	0.44444
$\bar\Pi_{2,2}$ [6]	0	0	0	0	0.11111	0.11111	$\bar\Pi_{2,2}$ [6]	0.44444	0.44444
$\bar\Pi_{2,3}$ [4]	0	0	0	−1	0.11111	0	$\bar\Pi_{2,2}$ [3]	0.44444	0.55556
$\bar\Pi_{2,4}$ [3]	0	−1	−0.33333	1	0.11111	−0.33333	$\bar\Pi_{2,3}$ [24]	0.44444	0.41667
$\bar\Pi_{2,5}$ [12]	0	0	0	0	0.11111	0.11111	$\bar\Pi_{2,4}$ [6]	0.44444	0.55556
$\bar\Pi_{2,6}$ [12]	0	0	0	0	0.11111	0.11111	$\bar\Pi_{2,4}$ [12]	0.44444	0.50000
$\bar\Pi_{3,1}$ [12]	0	0	0	0	0.03704	0.11111	$\bar\Pi_{2,5}$ [24]	0.44444	0.36111
$\bar\Pi_{3,1}$ [8]	0	0	0	0	0.03704	0	$\bar\Pi_{3,1}$ [8]	−0.29630	−0.33333
$\bar\Pi_{3,2}$ [24]	0	0	0	0	0.03704	0	$\bar\Pi_{3,2}$ [12]	−0.29630	−0.33333
$\bar\Pi_{3,3}$ [3]	0	0	0	0	0.03704	−0.11111	$\bar\Pi_{3,2}$ [12]	−0.29630	−0.33333
$\bar\Pi_{3,3}$ [12]	0	0	0	0	0.03704	−0.11111	$\bar\Pi_{3,3}$ [48]	−0.29630	−0.25000
$\bar\Pi_{3,3}$ [12]	0	0	0	0	0.03704	−0.33333	$\bar\Pi_{3,3}$ [24]	−0.29630	−0.30556
							$\bar\Pi_{3,3}$ [24]	−0.29630	−0.27778
							$\bar\Pi_{3,3}$ [24]	−0.29630	−0.27778
							$\bar\Pi_{3,3}$ [24]	−0.29630	−0.38889
							$\bar\Pi_{3,3}$ [8]	−0.29630	−0.25000
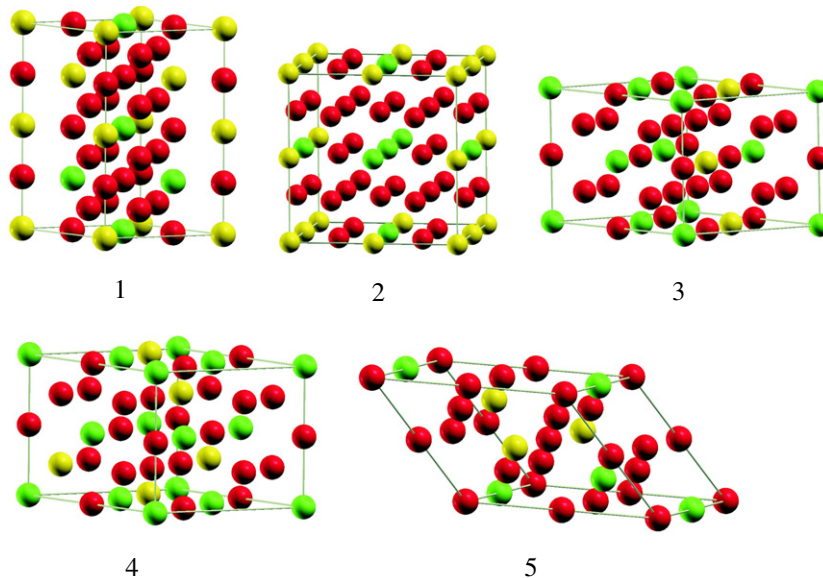
Fig. 1. The pictures of the SQSs. (1) $A_3(B_{1/2}C_{1/2})$, SQS-8 (2) $A_3(B_{1/2}C_{1/2})$-cubic, SQS-8 (3) $A_3(B_{1/3}C_{2/3})$, SQS-6 (4) $(A_{5/6}B_{1/6})_3C$, SQS-18 (5) $A_3(B_{1/2}C_{1/2})$, SQS-4. Red, yellow and green spheres represent A, B and C atoms, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

smallest correlation functions error up to the eighth-nearest neighbor pairs and the third-nearest neighbor triples. The structure is identical with SQS-1 generated by Jiang [21], which has a face-centered orthorhombic structure (space group Cmmm NO. 65). At $x = 1/3$, a primitive monoclinic structure (space group P2-1/m NO. 11) was obtained for $N = 6$. Besides, for $(A_{1−x}B_x)_3C$ at $x = 1/6$, we search the structures whose pair correlation functions are identical to those of the random alloy up to the first-nearest neighbor, and 204 structures were gained for $N = 18$. The structure was selected with the smallest correlation functions error up to the fifth-nearest neighbor pairs and the third-nearest neighbor triples. The ideal structure has a primitive triclinic structure (space group P1 NO. 1).

2.2. First-principles calculations

A plane wave basis was used to expand the electronic wave functions, as implemented by the ABINIT package. Norm-conserving pseudopotentials generated according to Troullier–Martins scheme were used within the local density approximation (LDA) for the ex-change correlation energy functional. A kinetic-energy cutoff of 30 Hartree was set. The irreducible Brillouin-zone (IBZ) integrations were performed on the **k**-point sets generated automatically in the Monkhorst–Pack scheme. We employed 0.005 Hartree Fermi–Dirac smearing of occupation number around the Fermi surface. A convergence test was carried out by using different **k**-point meshes and the kinetic-energy cutoff to keep the total energy error with 0.3 kJ/mol. All the SQSs were optimized by the Broyden-Fletcher-Goldfarb-Shanno (BFGS) minimization method, with respect to both the volume and the shape of the unit cell as well as the atomic positions.

3. Results and discussions

3.1. Convergence test

The more atoms the SQSs contain, the better approximations of the random alloys will be obtained. As a result, it is import to test the convergence of SQSs with N from the total energies of various