First-principles investigation of the Al–Si–Sr ternary system: Ground state determination and mechanical properties

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ABSTRACT

Twelve different ternary phases of the Al–Si–Sr system were characterized using first-principles calculations based on Density Functional Theory. Two different exchange correlation functionals were considered to extract its influence on the global results. In addition to the four phases (AlSiSr, Al_2Si_2Sr, $Al_2Si_2Sr_3$ and $Al_{16}Si_{30}Sr_8$) reported for this system, we explored eight other ternary phases ($Al_2Si_3Sr_3$, $Al_2Si_4Sr_3$, $Al_2Si_7Sr_5$, $Al_3Si_7Sr_{10}$, $Al_6Si_3Sr_{20}$, $Al_6Si_9Sr_{10}$, $Al_8Si_3Sr_{14}$ and $AlSi_6Sr_4$) that has been reported in chemically analogous systems. The mechanical stability of the phases was determined through the analysis of the elastic constants, and the energetic stability was established using the calculated formation enthalpy. The thermodynamic and vibrational properties of the AlSiSr, $Al_2Si_2Sr_3$ and $Al_2Si_4Sr_3$ phases were studied considering the harmonic, quasi-harmonic as well as simple anharmonic corrections. All phases were found to be stable, except for the $AlSi_6Sr_4$ and $Al_6Si_9Sr_{10}$. An isothermal section of the phase diagram was calculated at 0 K with the Thermocalc software, where it was found that the $Al_2Si_4Sr_3$ and $Al_6Si_3Sr_{20}$ phases can belong to the ternary ground state. The surface energy sections show that the other phases are metastable with a $\Delta G_{0\ K} \approx 2$ kJ/mol–atom, all stables and metastable phases show a metallic behavior and high compressibility.

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1. Introduction

The Al–Si–Sr system is very important in the light-metal alloys industry. In Al–Si cast alloys, for example, strontium is used as a modifier of the Al–Si eutectic [1]. When small quantities of strontium (hundreds of ppm at most) are added to Al–Si eutectic alloys, the morphology of the silicon crystallites change dramatically, from an acicular to a fibrous morphology. This morphological change refines the microstructure, which in turn results in much better mechanical and structural properties [2]. Furthermore, recent work on Al–Mg alloys that use silicon as an alloying element, shows that strontium improves fatigue resistance at high temperatures [3–5]. Therefore, a deeper understanding of the Al–Si–Sr ternary system is important for the further development of these classes of light metal alloys, which have received considerable attention in recent years.

An in-depth study of the phase stability of the Al–Si–Sr ternary is further justified by considering that several intermetallic

compounds in this system are being studied for different applications: AlSiSr for its superconducting behavior [6,7], the non-stoichiometric $SrAl_2$ [8] for its potential as a hydrogen storage material and the Al_2Si_2Sr [9] and $Al_{16}Si_{30}Sr_8$ [10] phases for their thermoelectric properties. All of the previously mentioned phases have yet to be studied completely and outside of these compositions there is little theoretical or experimental information available.

Investigations on the phase stability of chemically-related systems suggest that it may be possible to find new intermetallic compounds in regions of the Al–Si–Sr phase diagram that are yet to be investigated in detail. Specifically, studies on the Al–Ge–Ba, Al–Ge–Ca, Al–Ge–Sr, and Al–Si–Mg systems report the existence of several ternary intermetallic phases that could also be stable in Al–Si–Sr. Table 1 shows the crystallographic information of eight intermetallics structures observed in the four systems already mentioned along with the structures reported for the Al–Si–Sr system. The structures with space group $P-6m2 \Leftrightarrow p6/mmm$, $P-3m1$ and $Immm$ are present in Al–Si–Ca, Al–Ge–Ba, Al–Ge–Sr and Al–Si–Sr ternary systems [6,11–14] and have similar properties due to the affinity between the elements of the group *IV* and the rare-earth elements. The fact that these three structures are

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Table 1
Crystallographic information of the intermetallics phases in systems chemically analogous to Al–Si–Sr.

Phase	Space group		Pearson Symbol	Cell Parameters		
	Number	Symbol		a	b	c
$AlSi_6Mg_4$ [15]	12	$C2/m$	mC11	16.53	3.63	6.72
$Al_2Ge_3Ca_3$ [16]	62	$Pnma$	oP8	11.39	4.34	14.83
$Al_6Ge_9Ca_{10}$ [17]	166	$R-3m$	hR35	13.98	13.98	21.07
$Al_6Ge_{13}Ca_{20}$ [17]	176	$P63/m$	hP39	16.00	4.58	16.00
$Al_2Ge_4Sr_3$ [17]	12	$C2/m$	mC9	12.67	4.16	8.87
$Al_8Ge_3Sr_{14}$ [18]	148	R-3	hR35	11.96	11.96	40.10
$Al_2Ge_7Ba_5$ [12]	12	$C2/m$	mC14	8.59	10.31	18.47
$Al_3Ge_7Ba_{10}$ [19]	193	$P63/mmm$	hP20	9.74	9.74	16.47
$Al_{16}Si_{30}Sr_8$ [14]	223	$Pm-3n$	cP54	10.47	10.47	10.47
$AlSiSr$ [14]	187	$P-6m2$	hP3	4.23	4.23	4.74
Al_2Si_2Sr [14]	164	$P-3m1$	hP5	4.18	4.18	7.41
$Al_2Si_2Sr_3$ [14]	71	$Immm$	oI7	4.07	4.82	18.99

common to all these ternary systems suggests that structures with the same symmetry and stoichiometry may also be present in the Al–Si–Sr system.

The aim of this study is to investigate the possible existence of new phases in the Al–Si–Sr ternary system. In order to achieve this, we investigate the stability of those phases, considering both energetic and mechanical criteria. The energetic stability is evaluated considering the enthalpy of formation of the intermetallics calculated from first-principles at 0 K. In this case, there are no entropic contributions and the free energy simply corresponds to the enthalpy. This methodology was used in the case of the binary intermetallics of the Al–Sr [20] and Sr–Si [21] systems. In those cases as well as in this work, first-principles calculations were combined with the CALPHAD approach [22] to obtain the ground state and corresponding low-temperature phase diagram of the system. The phases under consideration include the known intermetallics in the Al–Si–Sr system, as well as those with the same symmetry observed in Al–X–Y (X = Si,Ge Y = Mg,Ca,Sr,Ba) systems (see Table 1). We report on the total energy calculations as well as on the formation enthalpy of these structures. The stability of these structures were further investigated by considering mechanical stability conditions in terms of the elastic tensor [23]. This analysis allowed us to determine whether any of these phases were unstable and thus not likely to form even under non-equilibrium (metastable) conditions. Finally, for two intermetallic compounds that belong to the ternary ground state, we calculated the vibrational and thermodynamic properties at finite temperatures.

The paper is organized as follows: Section 2 contains a description of the methodology used as well as the details of the first-principles calculations performed. The results and discussion of the stability and possible existence of new phases is presented in Section 3, as well as a detailed theoretical description of the stable intermetallics. The discussion of the vibrational properties for the AlSiSr, $Al_2Si_2Sr_3$ and $Al_2Si_4Sr_3$ intermetallics is presented in Section 4, and the conclusions of the paper are included in Section 5.

2. Methodology

2.1. Total energy calculations

The total energy calculations were performed within the framework of the Density Functional Theory [24], as implemented in the Vienna Ab Initio Simulation Package (VASP) [25,26]. Two approximations for the exchange correlation were considered: the Local Density Approximation (LDA) according to the Perdew–Zunger parameterization [27] and the Generalized Gradient Approximation (GGA) in the form of PW91 [28]. Wave functions

were expanded in plane waves, using the $Al:3s^23p^1$, $Si:3s^23p^2$ and $Sr:4s^24p^65s^2$ electronic configuration for the valence electrons described within the projector augmented-wave (PAW) pseudo-potentials formalism [29], implemented in the VASP package. The Brillouin zone integrations were performed using a MonkhorstPack mesh [30]. Full relaxations were realized by using the Methfessel–Paxton smearing method of order one [31] and a final self-consistent static calculation with the tetrahedron smearing method with Blöchl corrections [32]. To ensure the convergence in energy to better than 1 meV and 1 kBar in pressure, we used an energy cut-off of 350 eV and a k-point grid sets according to Table 2.

2.2. Elastic constants calculations

The elastic constants of all the intermetallic compounds considered in this work were calculated using the efficient strain-stress method [33], where a set of strains $\varepsilon = (\varepsilon_1,\varepsilon_2,\varepsilon_3,\varepsilon_4,\varepsilon_5,\varepsilon_6)$ is imposed on a crystal structure. If A is the lattice vectors specified in Cartesian coordinates, $\varepsilon_1,\varepsilon_2,\varepsilon_3$ and $\varepsilon_4,\varepsilon_5,\varepsilon_6$ are the normal strains and the shear strains respectively. Then, the deformed lattice vectors are:

$$\overline{A} = A \begin{pmatrix} 1+\varepsilon_1 & \dfrac{\varepsilon_6}{2} & \dfrac{\varepsilon_5}{2} \\ \dfrac{\varepsilon_6}{2} & 1+\varepsilon_2 & \dfrac{\varepsilon_4}{2} \\ \dfrac{\varepsilon_5}{2} & \dfrac{\varepsilon_4}{2} & 1+\varepsilon_3 \end{pmatrix} \quad (1)$$

After the application of the strain, it is possible to obtain the set of stresses t, which result from the changes on the energy due to the deformation, which is obtained from the electronic structure calculations. Applying Hooke's Law ($t = \varepsilon C$), if a n set of strains ($\varepsilon_{1 \to n}$) are applied, the result is n set of stresses ($t_{1 \to n}$) which can be used to find the 6×6 elastic constant matrix (C) according to:

$$\begin{pmatrix} C_{11} & \cdots & C_{16} \\ \vdots & \ddots & \vdots \\ C_{61} & \cdots & C_{66} \end{pmatrix} = \begin{pmatrix} \varepsilon_{1,1} & \cdots & \varepsilon_{1,n} \\ \vdots & \ddots & \vdots \\ \varepsilon_{6,n} & \cdots & \varepsilon_{6,n} \end{pmatrix}^{-1} \begin{pmatrix} t_{1,1} & \cdots & t_{1,n} \\ \vdots & \ddots & \vdots \\ t_{6,1} & \cdots & t_{6,n} \end{pmatrix} \quad (2)$$

The elements in the C tensor are written as C_{ij} according to the Voigt's notation and the linearly independent sets of strains necessary to calculate the elastic constants can be written of the following way:

$$\varepsilon = \begin{pmatrix} x_{11} & 0 & 0 & 0 & 0 & 0 \\ 0 & x_{22} & 0 & 0 & 0 & 0 \\ 0 & 0 & x_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & x_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & x_{55} & 0 \\ 0 & 0 & 0 & 0 & 0 & x_{66} \end{pmatrix} \quad (3)$$

According to the symmetry of the structure, the minimum number of linearly independent sets of strains that can be used to determine the elastic constants are two for cubic, three for

Table 2
Chosen K-points mesh for the intermetallics studied in this paper, according to a Gamma-centered (Γ) Monkhorst-Pack.

Phase	Mesh (k)	Phase	Mesh (k)
$AlSiSr$	$16 \times 16 \times 14$	$Al_2Si_7Sr_5$	$8 \times 8 \times 8$
Al_2Si_2Sr	$15 \times 15 \times 9$	$Al_3Si_7Sr_{10}$	$8 \times 8 \times 4$
Al_2SiSr_3	$12 \times 12 \times 12$	$Al_6Si_{13}Sr_{20}$	$4 \times 5 \times 15$
$Al_{16}Si_{30}Sr_8$	$4 \times 4 \times 4$	$Al_6Si_9Sr_{10}$	$6 \times 6 \times 6$
$Al_2Si_3Sr_3$	$6 \times 15 \times 4$	$Al_8Si_{13}Sr_{14}$	$6 \times 6 \times 6$
$Al_2Si_4Sr_3$	$12 \times 12 \times 9$	$AlSi_6Sr_4$	$9 \times 9 \times 12$