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The structural and compositional evolution of precipitates in Al-Mg-Si-Cu alloy

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ABSTRACT

The structural and compositional evolution of precipitates in Al-Mg-Si-Cu alloys were systematically investigated by atomic resolution high-angle annular dark-field scanning transmission electron microscopy and atom probe tomography. In under-aged alloys, most of precipitates have a disordered structure, with a substructure of β″ (LDC) and Cu sub-unit cluster or C unit cell. After aging to peak strength, disordered precipitates including β″, QP1 and QP2 phases are formed. The disordered QP1 and QP2 phases, which contain the unit cells of Q′ and C phases, respectively, are the precursor phases of Q′ phase in these alloys. The β″ phase can transform into the disordered QP1 phase by incorporating Cu atoms, forming Cu sub-unit clusters and QP lattice. When the alloy is over-aged, the ordering and transformation of QP1 to Q′ occurs by the formation of Cu sub-unit clusters, the ordering of QP lattice, and the ordering of QC lattice. In contrast, the transformation of the disordered QP2 phase are rather sluggish. After sufficient aging, Q′, C and disordered QP2 transform into the Q phase. During the evolution of the precipitates in these alloys, a continuous incorporation of Mg, Si and Cu atoms and release of Al atoms occur. These findings provide new insights in understanding precipitation in Al-Mg-Si-Cu alloys.

1. Introduction

Heat-treatable Al-Mg-Si-(Cu) alloys are important in a wide range of industrial applications, including automotive, aircraft, and architecture [1,2]. These alloys display a large increase in strength upon aging at elevated temperatures due to the formation of nanosized precipitates that disrupt dislocation movement [3,4]. The mechanical properties of these alloys can be significantly modified by controlling the size, type, orientation and distribution of these precipitate particles. For Al-Mg-Si alloys, the precipitation sequence is generally considered to be [5]:

SSSS → atomic clusters → GP zones → β″ → β′, U1, U2, B′ → β, Si

GP zones are the first distinct phases formed during aging and grow coherently with solute atoms ordered on Al lattice positions [6]. Chen et al. [7] reported that GP-zones evolved on Si_2 pillars providing structural stability for subsequent precipitates. The needle-like β″ phase is most efficient for strengthening these alloys and provides for maximum hardness. The atomic structure of β″ phase was investigated by Zandbergen et al. [8] using dynamic electron diffraction. They proposed that β″ has a composition of Mg_5Si_6 with a C-centered monoclinic unit cell of $a = 15.16$ Å, $b = 4.05$ Å, $c = 6.74$ Å and $\alpha = 105.3°$. Close-ups of the cross-section show that β″ is essentially a stack of identical units with an eye-like appearance. The structural unit, consisting of nine atomic columns with 4-fold symmetry, was referred to as a "low density cylinder" (LDC) in previous literature [6,9], as seen in Fig. 1(a). During over-aging, coarser post-β″ phases, such as β′, U1, U2 and B′, appear and are associated with a significant loss of strength [10–14]. The U1, U2 and B′ are also termed as Type A, Type B and Type C, respectively, as reported by Matsuda [10]. Table 1 gives an overview of precipitation phases in the Al-Mg-Si alloy as reported in the literature.

Cu addition can significantly increase the age hardening kinetics of Al-Mg-Si alloys. The precipitation sequence of Al-Mg-Si-Cu alloys is reported as [15].

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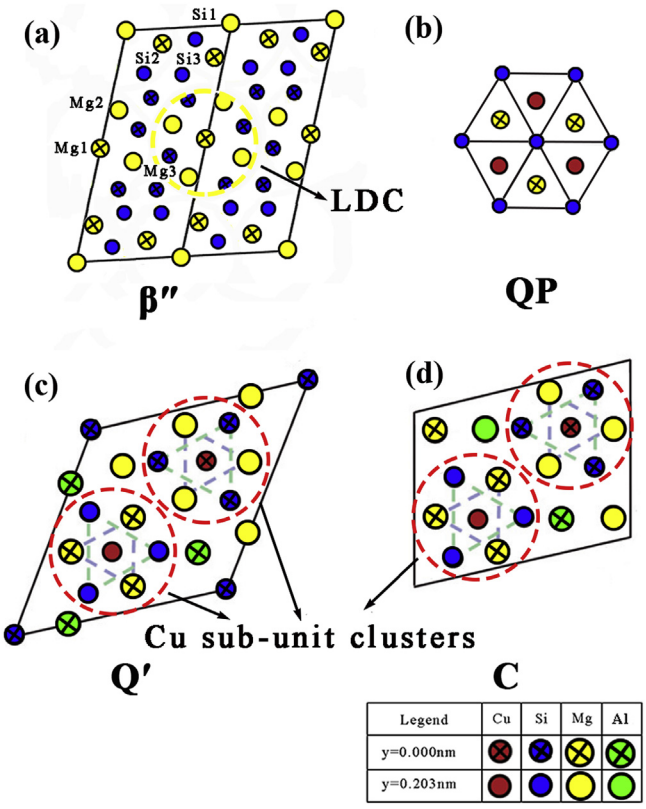

Fig. 1. Schematic illustration of the unit cells of (a) β″, (b) QP, (c) Q′ and (d) C phases. The substructure of β″ phase (LDC) is marked by dashed yellow circle, and the substructure of Q′ and C phases (Cu sub-unit clusters) is marked by dashed red circles. In the QP phase, the red and blue positions are actually occupied by a Cu and Si atoms with a probability of occupancy. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

SSSS →atomic clusters → GP zones → β^″, L/S/C, QP, QC → β′, Q′ → Q, Si

The addition of Cu decreases the precipitation of β″, and results in the formation of quaternary Q phase and its precursors during aging. Detailed TEM work by Cayron et al. [16,17] on Al-Mg-Si-Cu alloys, derived from reactions in metal matrix composites, revealed several metastable phases in the precipitation sequence: the hexagonal QP ($a = 3.93$ Å, $c = 4.05$ Å) at peak age, the hexagonal QC ($a = 6.7$ Å, $c = 4.05$ Å) after over-aging, and the hexagonal Q′, which leads to the formation of equilibrium Q phase after sufficient over-aging. These three phases are based on the same basic lattice, i.e., the QP lattice. The phase transition (QP → QC → B′ (Q′) → Q) can be understood as an atomic ordering process within the basal plane of the hexagonal lattice. Segalowicz et al. [18] reported a lath-shaped phase L to occur at peak aging along with β″, for which only the lattice parameters were provided. This L phase is different from Q′ and eventually transforms to Q. Marioara et al. [15] also investigated Cu addition to Al-Mg-Si-(Cu) alloys, finding that three kinds of Q′ precursors (L, S and C phases) with lath or plate morphologies are the most common precipitates formed during peak aging. β″ accounts for only 20%–30% of all the precipitates observed. The C phase has a plate-like morphology with a rectangular cross-section along <100>$_\alpha$. The structure is monoclinic with lattice parameters of $a_C = 10.32$ Å, $b_C = 8.10$ Å, $c_C = 4.05$ Å and $\alpha = 100.9°$. The composition of the C phase was identified as $Mg_4Al_1Si_{3+x}Cu_{1-x}$, with x~0.3 [19]. The L precipitate was proposed to be a disordered version of the C phase with a lath morphology, which contributes significantly to the hardening effect [20,21].

Q′ is a precursor to the equilibrium Q phase with a similar crystal structure. It is lath- or rod-shaped, with a hexagonal unit cell of $a_{Q'} = 10.32$ Å and $c_{Q'} = 4.05$ Å [22]. It has been reported that the orientation relationship (OR) between the lath Q′ and the matrix is $[1000]_{Q'}//[001]_\alpha$ and $(11\bar{2}0)_{Q'}//(510)_\alpha$ [23,24], and that there are multiple ORs between the rod Q′ and the matrix [23]. The equilibrium Q phase has the same morphologies and ORs as Q′ [22,25,26], and its lattice parameters are $a_Q = 10.39$ Å and $c_Q = 4.02$ Å. The composition of Q phase has been reported by different researchers with a range of stoichiometries, such as $Al_4Cu_2Mg_8Si_7$ [25], $Al_5Cu_2Mg_8Si_6$ [16] and $Al_3Cu_2Mg_9Si_7$ [27]. The $Al_4Cu_2Mg_8Si_7$ gives better agreement between experimentally measured and calculated percentages [25]. Table 2 gives an overview of known precipitation phases in the Al-Mg-Si-Cu alloy.

The precipitation behavior in Al-Mg-Si-Cu alloys has been investigated using various characterization methods and the structural characteristics of most precipitates are well understood. However, some controversy still surrounds precipitate transformation mechanism in these alloys. The following questions are still unanswered:

(1) How do the structure and composition of precipitates in Al-Mg-Si-(Cu) alloys change during artificial aging?
(2) Why are disordered precipitates formed in Al-Mg-Si-(Cu) alloys? What is the ordering mechanism of these disordered precipitates?
(3) What are the structural details and transformation rules for β″ and Q′ phases?

In the present work, atomic-resolution HAADF-STEM and APT techniques were used to study precipitate transformation mechanisms in Al-Mg-Si-(Cu) alloys. The formation of various disordered precipitates and the ordering mechanism for these disordered precipitates during further aging are described. The roles of stable

Table 1
Overview of known precipitation phases in the Al-Mg-Si alloy.

Phase	Shape	Composition	Space group	Lattice parameter/Å	Reference
β″	Needle	Mg_5Si_6	Monoclinic C2/m	a = 15.16, b = 4.05, c = 6.74, β = 105.3°	Zandbergen [8]
β′	Rod	Mg_9Si_5	Hexagonal $P6_3/M$	a = 7.15, c = 12.15, γ = 120°	Jacobs [12]
U1	Needle	$MgAl_2Si_2$	Trigonal P3ml	a = b = 4.05, c = 6.74, γ = 120°	Andersen [14]
U2	Needle	$Mg_2Al_2Si_2$	Orthorhombic Pnma	a = 6.75, b = 4.05, c = 7.94	Andersen [13]
B′	Lath	$Mg_9Al_3Si_7$	Hexagonal P6	a = b = 10.4, c = 4.05, γ = 120°	Matsuda [10]
β	Plate	Mg_2Si	Cubic Fm3m	a = 6.34	Jacobs [12]