Phase Transformations in the Al-Li-Hf and Al-Li-Ti Systems

NANCY F. LEVOY and JOHN B. VANDERSANDE

Phase transformations in Al-1.9Li-1.6Hf and Al-1.5Li-0.7Ti (wt pct) alloys have been analyzed thoroughly using various electron microscopy techniques. An L12-ordered ternary Al3(Li,X) phase, or α′(X), forms in both alloys during heat treatment. The α′ forms as spherical precipitates by normal nucleation and growth and in the Hf alloy as filmaments by discontinuous precipitation. The X:Li ratio in these precipitates is found to be a function of the precipitation mode in the Hf alloy. α′ is coherent with the Al matrix and serves as a preferred nucleation site for the precipitation of the Al3Li or 6′ phase when the alloy is aged at 190 °C. The 6′, also L12-ordered, grows as continuous envelopes which completely enclose the α′ phase. An altered morphology predominates for α′(Ti) after extended heat treatment. The major feature of the altered morphology is the incorporation of spiralied dislocations at the α′/matrix interface, which act to ease the misfit between the α′(Ti) and the matrix. 6′ forms as caps on the altered α′(Ti) in areas away from the dislocations. Disruption of the 6′ envelopes is attributed to the strain fields and loss of coherency associated with the presence of interfacial dislocations and a possible local shift from L12 to DO22 ordering in the α′(Ti) precipitates.

I. INTRODUCTION

Al-Li alloys offer a unique combination of reduced density, increased elastic modulus, and high strength, compared with conventional Al alloys. This combination of properties is especially attractive for structural applications in the aerospace industry.11 However, commercial applications have been limited thus far due to the low ductility and low fracture toughness of many Al-Li alloys.

The strength of Al-Li alloys is due to precipitation hardening by the metastable 6′ Al3Li phase. However, the nature of the 6′ phase also can contribute to poor fracture toughness in Al-Li alloys. 6′ is an ordered phase that forms as spherical coherent precipitates having a cubic:cube orientation with the α-Al matrix.2,3,4 6′ has a small negative lattice misfit with the α matrix,5 of −0.08 pct.2,3 Dislocation motion is accomplished by shearing of 6′ precipitates.6 Particle shearing in alloys strengthened by ordered precipitates weakens the plane on which shearing has occurred and results in intense planar slip.5 Planar slip leads to stress concentrations at the grain boundaries and premature intergranular failure.7,8

Mechanical property improvements in Al-Li alloys have been achieved by other researchers via rapid solidification techniques9 and by alloying additions which coprecipitate with δ110 or tie up Li in complex precipitates. The approach taken in the present work is based on the idea that resistance to precipitate shear can be increased by altering the basic precipitate morphology and precipitate composition in Al-Li through additions of Hf and Ti. Motivation for the present study comes in part from the recent work of Gayle11 which showed that additions of Zr to an Al-Li alloy modified the strengthening phase from δ′ Al3Li to a new ternary phase, Al3(Li,Zr), and that this modification resulted in significant improvements in strength and ductility.

The primary objective of the present work is to characterize the morphology, composition, and crystal structure of the precipitating phases in Al-Li-Hf and Al-Li-Ti alloys. Hf and Ti were chosen as alloying elements because each forms a precipitating phase in the Al-X system with the composition Al3X, and because the crystal structures and lattice parameters of Al3Hf and Al3Ti are similar to the structure and lattice parameter of Al3Li. The Al3Hf and Al3Li metastable precipitating phases are isostructural, both having the L12 (Cu3Au-type) ordered cubic structure (Figure l(a)). The precipitating Al3Ti phase has the tetragonal DO22 structure (Figure l(b)). The DO22 unit cell is composed of two distorted L12 subcells stacked one above the other along the [001] direction, with a shift of 1/2(110) on the (001) plane at their interface.12

II. BACKGROUND

A. Precipitation in the Al-X and Al-Li-X Systems, where X is Zr, Hf, or Ti

Aging behavior is similar in the Al-Hf and Al-Zr systems. The Al3Hf and Al3Zr phases form extensively during aging as discontinuously precipitated filaments or rods and as continuously precipitated spherical particles.13-17 The spherical and filamentary precipitates have a metastable L12 structure and are coherent with the α matrix.

The usual precipitating phase that develops during aging of an Al-low Ti alloy is the equilibrium Al3Ti phase with the DO22 structure.12,18,19 Precipitates of the Al3Ti phase have been described as globular or irregularly faceted platelets,12 laths and irregular plates,18 blocky, flake-like,20 and petal-like.20,21

During heat treatment of an Al-2.3Li-1.1Zr alloy at temperatures ranging from 450 °C to 580 °C, Li was found to substitute for Zr to form a ternary α′ or Al3(Li,Zr) phase.11 The ternary α′ phase forms discontinuously as rods and filaments and continuously as discrete spherical
B. Compositional Analysis of Li-Containing Phases

Standard techniques of microcompositional analysis are not presently capable of providing quantitative information about the Li composition in the α′ phase. For example, the technique of Energy Dispersive Spectroscopy (EDS) cannot detect the presence of Li in a sample, since the energy of the Li-K X-rays is below the detectability limit of available windowless detectors. Electron Energy Loss Spectroscopy (EELS) can be used to detect Li, but the ability of EELS to quantify Li content is limited due to a weak Li-K edge and interference of multiple plasmon scattering. The applicability of EELS to the present study is limited further by the fact that the minimum detectable Li content is several atomic percent.

A technique of compositional analysis by superlattice dark-field image calculation, developed by Gayle, is found to be the best available technique for the detection of Li in the precipitates of interest in this work. This technique will be reviewed in Section IV.

III. EXPERIMENTAL PROCEDURE

Alloys of nominal composition (in wt pct) Al-1.9Li-1.6Hf and Al-1.5Li-0.7Ti were produced by the rapid solidification process of melt spinning at the National Bureau of Standards (Gaithersburg, MD). Melt spinning conditions were optimized to balance two goals: (1) to maintain a solid solution of the alloying elements in the as-cast condition and (2) to produce alloy ribbons with sufficient thickness and width for easy thin-foil TEM sample preparation. Alloy ribbons were produced with a thickness of 60 to 100 μm and maximum width of 1 cm.

A two-step thermal treatment was used to control the precipitation reactions in the Al-Li-Hf and Al-Li-Ti melt spun alloys. The high temperature heat treatment was done in an argon atmosphere at 450 °C or 500 °C for periods of time from 10 minutes to 100 hours. During the high temperature treatment, a Hf- or Ti-rich phase precipitates. The low temperature heat treatment, or aging treatment, was done in air at 190 °C for periods of time from 0.5 to 115 hours. During the low temperature aging treatment, the α′ Al3Li phase precipitates.

Samples for Transmission Electron Microscopy (TEM) were prepared by standard techniques. The final thinning/polishing of the TEM samples was performed with a twin-jet electropolishing apparatus using a solution of 30 vol pct nitric acid in methanol at −20 °C. Microscopic examinations were done with a JEOL 200CX TEM.

IV. COMPOSITION BY IMAGE ANALYSIS AND CALCULATION

Superlattice dark-field image calculation is a useful method for determining the Li content of the α′ phase enveloped by the δ′ phase. Compositional determination by dark-field image analysis and calculation is based on the fact that the structure factor for a superlattice reflection of the L12-ordered α′ phase is a strong function of composition. Dark-field images are calculated as a function of composition by applying the kinematical theory of diffraction, in which the dark-field image intensity is proportional to the square of the structure factor. The remainder of this section gives a brief review of this method of composition determination.

A. Structure Factor Calculations

The structure factor, \( F_{hkl} \), of any unit cell can be written as

\[
F_{hkl} = \sum f_i \exp[-2\pi i(hu_i + kv_i + lw_i)]
\]  

where \( f_i \) is the atomic scattering amplitude for atom \( i \), and \( u_i, v_i, \) and \( w_i \) are the fractional coordinates of atom \( i \). The structure factor for a superlattice reflection of a perfectly ordered Al3X phase having the L12 structure (i.e., for mixed even and odd hkl) reduces to

\[
F_{hkl} = f_X - f_{Al}
\]