



Stabilizing the strengthening precipitates in aluminum-manganese alloys by the addition of tungsten



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ABSTRACT

The Al-Mn-W system has considerable potential as a basis for lightweight aluminum alloys that are intended for use at temperatures approaching 350 °C (623 K). In this ternary system, aluminum, manganese, and tungsten co-precipitate to form the meta-stable $\text{Al}_{12}(\text{Mn}_{(1-x)}\text{W}_x)$ phase, which is thermally stable and will not coarsen when held at elevated temperatures for extended periods of time. This enhanced thermal stability of the $\text{Al}_{12}(\text{Mn}_{(1-x)}\text{W}_x)$ phase in comparison to the Al_{12}Mn phase which forms in binary Al-Mn alloys is explained in terms of the Gibbs free energy of the two phases. It is shown that co-precipitating tungsten with aluminum and manganese lowers the Gibbs free energy of the precipitated phase and by so doing, it slows down its coarsening rate and enhances its thermal stability.

1. Introduction

Manganese has a relatively high solubility in aluminum compared to other transition metals (maximum solubility $\cong 1.2^1$ [1,2]), and it also has a relatively low diffusivity in aluminum ($D_{\text{Mn}} = 2.16 \times 10^{-6} \text{ m}^2/\text{s}$ at 450 °C (723 K) [3]). For these reasons, it is envisioned that lightweight aluminum alloys may be developed for high temperature applications on the basis of the Al-Mn system wherein an appropriate heat treatment causes precipitation of a strength-inducing Al-Mn phase. Aging homogenized Al-Mn alloys at a temperature between 400 °C (673 K) and 500 °C (773 K) may lead to formation of one or more different precipitate phases, including an orthorhombic phase with the chemical formula Al_6Mn , a body-centered cubic (BCC) phase with the chemical formula Al_{12}Mn (usually referred to as G), a simple cubic phase (usually referred to as G'),² and a hexagonal phase (usually referred to as G'') [4]. Of these precipitate phases, Al_6Mn is the equilibrium one and the others are all meta-stable phases. The G phase in particular is an attractive strength-inducer. It is semi-coherent with its surrounding aluminum matrix, and it tends to form with a prism-like morphology that is approximately 500 nm in equivalent length. Unfortunately, the G phase is meta-stable, and when it is subjected to elevated temperature for an extended period of time, it tends to coarsen and transform to the equilibrium Al_6Mn phase [2,5]. This transformation is invariably accompanied by significant loss of alloy strength. It has been shown that in many instances, it is possible

to stabilize binary Al_xTM_y (TM \equiv transition metal) precipitates by alloying into them other transition metals so that they form as ternary co-precipitates of the composition $\text{Al}_x(\text{TM}_1\text{TM}_2)_{1-y}$ [6,7]. Examples of phase stabilization by co-precipitation include co-precipitating zirconium with scandium to form $\text{Al}_3(\text{Sc}_x\text{Zr}_{1-x})$ [8–11], and introducing rare earth elements into Ni_3Al [12]. These 'precipitate stabilizing' elements usually have very low diffusivity in aluminum and thus the co-precipitated particles tend to resist coarsening. We believe that adding tungsten to binary Al-Mn alloys may stabilize the G phase relative to the Al_6Mn equilibrium phase by co-precipitating with manganese to form $\text{Al}_{12}(\text{Mn}_x\text{W}_{1-x})$ particles. Co-precipitation of tungsten and manganese is envisioned because both the Al_{12}W and the Al_{12}Mn phases have the same crystal structure (BCC), and their lattice parameter differs from one another by only 1.47% ($a_{\text{Al}_{12}\text{Mn}} = 0.747 \text{ nm}$ and $a_{\text{Al}_{12}\text{W}} = 0.758 \text{ nm}$ [13]). In this publication, we report on the effects of adding tungsten to binary Al-Mn alloys by measuring the alloy's ambient temperature tensile properties and correlating these measurements to the alloy's microstructure and to the coarsening kinetics of the strength-inducing $\text{Al}_{12}(\text{Mn}_x\text{W}_{1-x})$ precipitate particles.

2. Materials and procedures

Al-2Mn and Al-2Mn-0.8W alloys were constituted from pure aluminum ingots (99.99% purity), Al-25Mn-0.12Fe master alloy, and pure, 325 mesh tungsten powder. The alloys were melted in an

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¹ All compositions are in weight percent unless otherwise stated.

² The G' phase is believed to have the chemical formula $\text{Al}_{12}\text{Mn}_3\text{Si}$, and so it is not observed in Al-Mn alloys except when silicon is present [4].

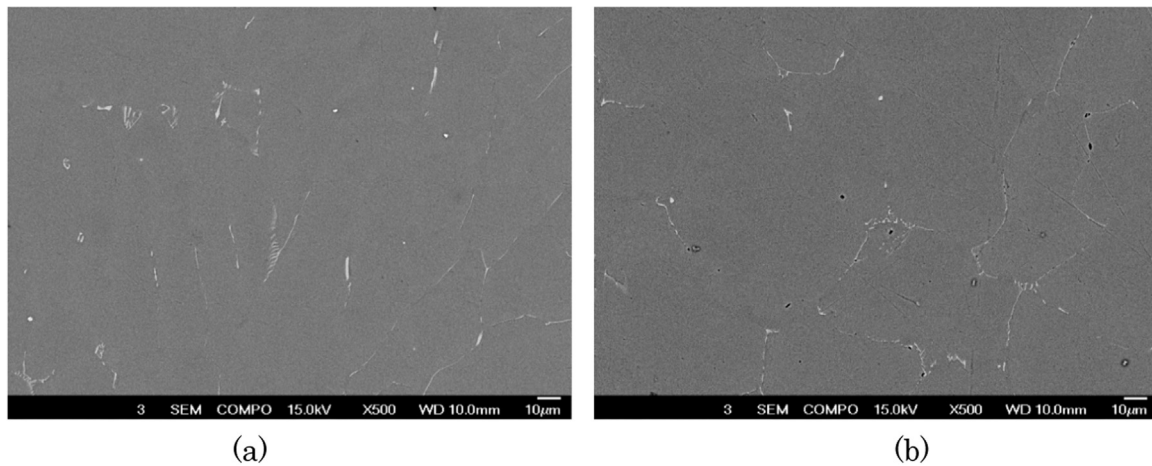


Fig. 1. SEM photomicrographs of as-cast (a) Al-2Mn, and (b) Al-2Mn-0.8W alloys.

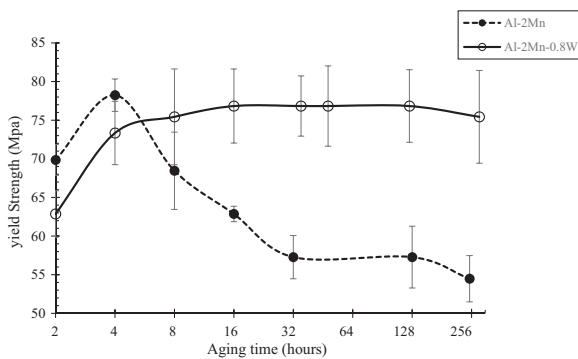


Fig. 2. Variation in measured yield strength of Al-2Mn and Al-2Mn-0.8W alloys with holding time at 450 °C (723 K).

induction furnace in clean silicon carbide crucibles that are coated with boron nitride. The melts were degassed with high purity argon gas by means of a rotating impeller degasser for 30 min, and then they were poured at approximately 850 °C (1123 K) into a water-chilled copper mold. The water-chilled copper mold produces standard ASTM sub-size tensile specimens with a uniform cooling rate of about 120 °C/s. The specimens were isothermally aged in an electric furnace and then they were cooled from the aging temperature to room temperature in still ambient air. Although precipitation hardenable aluminum casting alloys are typically solution heat treated and quenched before they are artificially aged, the Al-2Mn and Al-2Mn-0.8W alloys of this study were aged without solutionizing and quenching. This deviation from the norm is dictated by the fact that these alloys are based on peritectic systems wherein a solutionizing heat treatment is not possible without causing incipient melting of the cast part. For these alloys, it is submitted that the liquid is homogenized during melting and the fast cooling rate during solidification replaces the quenching step and preserves the homogeneous super saturated solid solution. As seen in Fig. 1, microstructure analysis shows that this statement is indeed true.

Samples from both alloys were prepared for scanning electron microscopy (SEM) by polishing according to standard metallographic methods. Samples used for transmission electron microscopy (TEM) were produced by thinning foils of the alloys to perforation by means of a twinjet electro-polisher (Fischione Instruments, model 120) operating at 12 V and utilizing a solution of 10 vol% perchloric acid in methanol maintained at -20 °C (253 K). A JOEL-7000F scanning electron microscope operating at 15 kV and a JOEL-2010F transmission electron microscope operating at 200 kV were used for microstructure analyses.

Room temperature tensile properties of the alloys were measured by means of a Universal Testing machine (Instron model 5500R) at an

extension rate of 0.05 in./min. A 1-in. gage length extensometer (MTS model 634.25E-24) was used to measure extension. At least 3 specimens were used in each measurement and the results were averaged and the standard deviations were calculated. Fracture of all specimens took place within the gage length and specimens with severe porosity and/or oxides that would affect the results were excluded from the analysis.

3. Results

3.1. As-cast microstructure

Fig. 1 shows SEM photomicrographs of the as-cast Al-2Mn and Al-2Mn-0.8W alloys. Nearly all the manganese and tungsten are solutionized in the α -Al matrix due to the high cooling rate during solidification. Only a small amount of manganese and iron segregates to the grain boundaries where it forms an Al-Mn-Fe compound as confirmed by Energy Dispersive Spectrometry (EDS).

3.2. Aging response of Al-2Mn and Al-2Mn-0.8W alloy

Fig. 2 shows the variation in measured yield strength of Al-2Mn and Al-2Mn-0.8W alloys with holding time at 450 °C (723 K). The Al-2Mn alloy reaches its peak yield strength of 78 MPa after 4 h and then its yield strength decreases quickly so that after 250 h it drops by about 28% from its maximum value. On the other hand, the measured yield strength of the Al-2Mn-0.8W alloy reaches its maximum value of 76 MPa after 12 h and stabilizes at this value for the duration of the test (more than 250 h).

3.3. Microstructure of isothermally held (400 °C) Al-2Mn and Al-Mn-0.8W alloys

Fig. 3 shows typical TEM photomicrographs of Al-2Mn and Al-2Mn-0.8W alloy samples that were isothermally held at 400 °C (673 K) for 4 h. The precipitates in both alloys appear to have irregular shapes. This is because they are not fully coherent with the α -Al matrix, and so they present different orientations to the field of vision. Fig. 4(a) and (b) show the select area diffraction pattern of precipitates from the $[210]_p$ zone axis in Al-2Mn and Al-2Mn-0.8W samples, respectively. The diffraction patterns indicate that the precipitates in both alloys have the BCC crystal structure. Ens. [4] identified the precipitate in the Al-2 wt%Mn alloy as metastable $Al_{12}Mn$ and referred to it as G phase. He reported its lattice parameter to be 0.747 nm [13], which is in agreement with measurements in Fig. 4(a). However the lattice parameter of precipitates in Al-2Mn-0.8W alloy is slightly larger than 0.75 nm, which may be caused by the dissolution of W element in

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