Suppression of Samson Phase Formation in Al-Mg Alloys by Boron Addition

R. Goswami* and S. B. Qadri

Materials Science and Technology Division
Naval Research Laboratory, Washington DC 20375, USA

Abstract

Al-Mg alloys, particularly Al 5083 and Al 5456, are widely used for boat and ship structural applications because of their unique properties such as lightweight, high strength and good weldability. However, structural parts manufactured with these alloys fail catastrophically as a result of the formation of Al_3Mg_2 , known as Samson phase, at grain boundaries. Here we demonstrate that the Samson phase formation is suppressed in Al 5083 by alloying with B, which traps most of Mg in solid solution as AlMgB_2 phase. This decreases the supersaturation level of Mg in Al matrix, which is a driving force for the formation of Samson phase in Al 5083. We observe Cu-rich precipitates, instead of the Samson phase, at grain boundaries upon extended annealing at 150°C. This is a significant finding as it provides new insight as to how to minimize the longstanding problem of sensitization.

Key words: Al-Mg alloys, Sensitization, Samson Phase, Grain boundary precipitation, TEM

1. Introduction

Considerable work has been done on the complex Al_3Mg_2 intermetallic compound, known as Samson phase [1]. It is a cubic structure with space group: $m\bar{3}m$, lattice parameter 28.239Å and 1170 atoms per unit cell. In Al-Mg alloys, particularly in Al 5083 and Al 5456, this phase precipitates out from the supersaturated Al-Mg solid solution as a result of thermal exposure in the range of 50-200°C [2,3,4,5]. It mostly forms at grain boundaries in Al-Mg alloys, which makes them susceptible to intergranular corrosion (IGC) and stress corrosion cracking (SCC) as the grain boundary intermetallic phase is highly anodic relative to the Al matrix. This leads to a catastrophic structural failure via anodic dissolution of the grain boundary phase upon exposure to seawater and stress [3]. It is a longstanding problem of naval vessels, which use Al 5000 series alloys in order to decrease the overall weight and fuel consumption, and to increase the speed.

Recently, different thermo mechanical treatments [6], alloy additions of Sr, Nd and Zn [5,7,8] and local reversion of thermal treatments [9] have been applied to minimize the formation of the grain boundary Samson phase and sensitization. However, these methods are not effective in preventing the formation of grain boundary Al_3Mg_2 . We report here for the first time the prevention of this phase at grain boundaries in Al 5083 by alloying with B and Cu that reduces the supersaturation of Mg, which is the thermodynamic driving force for the precipitation of Al_3Mg_2 in Al matrix. Small additions of boron have been reported to enhance the creep-rupture resistance of superalloys [10]. Usually boron in superalloys segregates to grain boundaries because of its large size misfit with nickel and modifies the grain boundary chemistry.

* Corresponding author, e-mail: ramasis.goswami@nrl.navy.mil

2. Experimental

An ingot with Al-5083 with some amount of B and Cu was produced by arc melting in an inert atmosphere. Such ingot was melted several times to ensure the homogeneity, and allowed to cool in the furnace. We have added ≈ 2.0 wt.% B and ≈ 0.75 wt.% Cu to Al 5083, which contains ≈ 94 wt. % Al, ≈ 4.5 wt. % Mg and small amount of Mn, Fe and Cr. The ingot was homogenized at 500°C for 2h and annealed at 150°C for ≈ 190 h. Samples for TEM were prepared using an ion mill with a gun voltage of 4 kV for each gun, and a sputtering angle of 10° . A JEOL-2200FX analytical transmission electron microscope was then employed to examine the microstructure and composition. Fine-probe energy dispersive X-ray spectroscopy (EDS) was used to determine the distribution of B, Cu and Al. Further compositional information was obtained with high-angle annular dark field (HAADF) imaging. For structural analysis, we use x-ray diffraction (XRD) using Rigaku diffractometer utilizing Cu $K\alpha 1$ radiation.

3. Results and Discussion

Boron is known to form di-boride compounds, MgB_2 and AlB_2 , with Mg and Al, respectively. These di-boride compounds crystallize in hexagonal (P6/mmm) structure with lattice parameters, $a = 3.08 \text{ \AA}$ and $c = 3.51 \text{ \AA}$ for MgB_2 , $a = 3.01 \text{ \AA}$ and $c = 3.24 \text{ \AA}$ for AlB_2 . In the present work, however, the ternary Al-Mg boride particles, as evidenced by XRD and TEM, form in Al matrix. As the MgB_2 and AlB_2 have the same structure, one would expect solubility of Mg in AlB_2 lattice, and it is more likely to substitute the Al atoms in the AlB_2 lattice.

Fig. 1(a) shows the HAADF image of one such rod-like boride particle in an Al matrix in the as-cast condition. The fine-probe EDS map shows that it is an Al-Mg ternary boride particle with considerable amount of Mg. The distribution of Al, Mg and B in the boride particle and matrix is shown in Fig.1 (b-e), respectively. A line scan, Fig. 1(f), across the particle shows considerable drop in Al counts close to the broad faces as compared to the core, suggesting that AlB_2 forms initially during solidification and then Mg diffuses through the broad faces. In addition, Cu-rich precipitates, appeared bright in the HAADF image, were observed on top of the boride particle.

X-ray diffraction (XRD), Fig. 2, clearly shows α -Al, Al_2Cu and AlMgB_2 phases upon extended annealing at 150°C of this alloy. Note that the peaks corresponding to $2\theta = 27.187$ and 56.14 have been shifted to the lower angles as compared to the 0001 and 0002 of AlB_2 , suggesting that the c-parameter increases as a result of insertion of Mg in AlB_2 lattice. In fact, the c-parameter of the boride phase is $3.28 \text{ \AA}$, while the a-parameter does not change significantly with respect to AlB_2 . Using Vegard's law, the ratio of Al and Mg in the ternary boride turns out to be $\approx 3:1$. Fig. 3 is a HRTEM image obtained from a portion of rod-like AlMgB_2 particle showing the lattice fringes of 0001, 10-10 and 10-11 planes close to the $[-12-10]$ zone. The corresponding fast Fourier transform (FFT) obtained from part of the image is given as a right inset, showing the 0001, 10-10 reflections with d-spacing $\approx 3.28 \text{ \AA}$ and $\approx 2.6 \text{ \AA}$, respectively, which is consistent with XRD observations.

In Al 5083, the Mg in solid solution strengthens the Al matrix through solid-solution hardening. The formation of AlMgB_2 in Al matrix decreases the Mg level in solid solution and reduces the strength. The addition of Cu, however, results in the formation of several Cu-rich nanocrystalline precipitates. Figs. 4 (a-d) show nanocrystalline Al_2Cu (θ'), Al_2CuMg (S-phase) [11] and Ω -phase [12] precipitates in the matrix upon extended annealing. All these Cu-rich precipitates enhance the strength of the alloy.

To study the grain boundary microstructure, we examined number of grain boundaries for samples annealed at 150°C for 190h in HAADF imaging mode. In this imaging mode, the brighter regions correspond to heavier atoms, as the scattering cross-section is proportional to Z^2 (atomic number). Fig. 4 (e) is a typical HAADF image showing the grain boundary precipitates. Most precipitates appeared bright in the HAADF imaging mode, suggesting that these precipitates are Cu rich. These precipitates are mostly S-phase. In the HAADF imaging mode, however, the Samson phase, Al_3Mg_2 , as it is enriched with Mg, appears darker as compared to the matrix [2,3,4]. We present the microstructure of the Samson phase at a grain boundary without the addition of B and Cu (see Fig. 4(f-i)) taken in HAADF mode from a highly sensitized Al 5083 (sensitized at 175°C for 240h) for comparison. Specifically, TEM observations revealed that the Mg rich β phase formed a continuous film at a number of grain boundaries after annealing the sample at 175°C. An EDS line scan, (see Fig. 4(g), extracted from a region indicated by arrow in Fig. 4(f), and the fine probe EDS maps of Mg and Al across this boundary showed the enrichment of Mg (Figs. 4h and 4i), respectively.

4. Summary and Conclusions

We demonstrated that the Samson phase formation in Al 5083 has been suppressed by alloying with B and Cu. TEM and XRD revealed that a ternary boride compound, AlMgB_2 , forms along with Cu-rich nanocrystalline precipitates in Al matrix. The AlMgB_2 phase formation decreases the supersaturation level of Mg in Al matrix, which is a driving force for the formation of Samson phase in Al 5083. Upon extended annealing at 150°C, we observe Cu-rich precipitates, instead of Samson Phase, at grain boundaries.

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Figure Captions

Fig. 1 (a) A HAADF image showing the rod like boride particle. (b-e) Fine probe EDS maps showing the distribution of B, Mg, Al and Cu, respectively. (f) A line-scan across the particle.

Fig. 2 XRD showing the AlMgB_2 and Al_2Cu precipitates in Al matrix. Inset shows the 10-11 boride peak.

Fig. 3 HRTEM image of the boride particle. A low magnification image of the particle and the FFT pattern are shown as left and right insets, respectively.

Fig. 4. TEM images showing different precipitates in Al matrix. a) Al_2Cu b) A multibeam image showing the S and T_1 precipitates. (c and d) HRTEM images of T_1 and S-phase close to $[11-2]$ zone of Al. The corresponding FFTs obtained from part of the matrix and precipitate are shown as insets. (e) A HAADF image showing Cu-rich precipitates at grain boundary for sample annealed at 150°C for 190h. (f) A HAADF image of grain boundary β -phase in sensitized Al 5083. (g) The Line scan across the interface showing the distribution of Al and Mg. (i) and (j) EDS maps of Mg and Al, respectively.

Fig. 1

Fig. 2

Fig. 3

Fig. 4