Characterization of precipitation in Al–Mg–Cu alloys by X-ray diffraction peak broadening analysis

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ABSTRACT

The present study examines the aging behavior of Al–Mg–Cu alloys based on the elastic effects on the matrix due to coherent precipitates; these effects were followed by X-ray diffraction peak broadening analysis. We conclude that the growing of matrix distortion zones around the precipitates is well described by the 2M *factors* established by Houska. In terms of mechanisms, in the first stages of ageing the rapid hardening seems to not be related with the interaction of dislocations with the stress field around the precipitates. The incremental microhardness observed in this alloy can be attributed to the formation of clusters or to solute-dislocation interactions.

1. Introduction

Recently, Al–Mg–Cu alloys have caused great interest in the automotive industry for potential use in car-body panels because they increase the paint–baking response without diminishing good formability, mechanical resistance and corrosion resistance of classical Al–Mg alloys. After stamping processes, the car parts must be assembled and painted. The paint–baking treatment is carried out between 150 to 180 °C for 20–30 min. Al–Mg alloys (AA5xxx series) lose part of their mechanical properties during the paint–baking treatment due to the recovery mechanism. Small additions of Cu improve the mechanical strength of Al–Mg alloys during these heat treatments by precipitation hardening [1–5].

Ratchev *et al.* claimed that the age-hardening behavior of Al–Mg–Cu alloys[1] is similar to that in the Al–Cu–Mg alloys[1–2]. These similarities include two stage-hardening. The first stage (rapid-hardening stage) is realized after only several minutes of ageing. The differences are associated with the behavior following the first stage where the Al–Cu–Mg alloys develop a plateau on the age hardening curve, whereas the Al–Mg–Cu alloys continue to harden at a relative low rate.

The correlation between the microstructural changes and the hardening behavior is still not clearly defined. According to Silcock, the rapid hardening stage was attributed to the homogeneous precipitation of GPB (Guinier–Preston–Bagaryatsky) zones [6]. Ringer *et al.* proposed a mechanism called "cluster hardening". According to this mechanism Mg–Mg, Cu–Cu and Mg–Cu clusters were responsible for the initial hardening, and GPB zones were detected later in the ageing process and were responsible for the second hardness increase [7–9]. Studies made by Charaï *et al.* indicated that clusters of Mg–Mg followed by Cu–Cu and Cu–Mg are formed during and immediately after quenching. These clusters induce an initial hardening effect for which the size of the Mg atoms seems to be a crucial factor [10]. Based on three-dimensional atom probe and transmission electron microscopy, Reich *et al.* revealed that a heterogeneous S-phase and clusters form after the rapid hardening stage, and

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[1] The notation "Al–Mg–Cu" implies that Mg is present in higher concentrations than Cu.

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solute segregation to existing dislocations causes dislocation locking and is responsible for the initial rapid hardening [11]. Later, the solute-dislocation interaction mechanism was supported by Nagai *et al.* with results obtained using the positron annihilation technique. [12].

The degree of strengthening obtained depends on the volume fraction and the size of particles, and on the nature of the interaction of the particles with dislocations (precipitate/matrix interface). In Al–Mg–Cu alloys the mechanical response is related to the distribution and evolution of the solute atoms (Mg and Cu) and to the nature of interfaces between metastable phases and the aluminum matrix.

Conventional Transmission Electron Microscopy (TEM) and High Resolution Electron Microscopy (HREM) are powerful tools for characterizing the microstructure (such as cell structure, morphology, orientation, etc.) of the intermediate phases in these alloys by direct observation. However, these techniques do not give information about the bulk sample. Moreover, sample preparation for TEM and HREM is highly time consuming and may induce changes in the defect structure during sectioning and polishing. On the contrary, the X-ray diffraction peak broadening analysis provides the microstructural parameters in a statistical manner (averaged over a volume of 10^9 μm^3). Moreover, the specimen preparation is less time consuming [13].

The shape and breadth of the X-ray diffraction profile are both determined by the mean crystallite size or distribution of sizes, and by the imperfections prevailing in the crystalline lattice. Hence, appropriate analysis of the line profile should yield such information as the mean crystallite dimension or size of the coherent crystalline domains, and the nature and extent of lattice imperfections [14]. The X-ray line profile analysis procedure can be used to analyze defects in the microstucture associated with precipitation phenomena. Such studies have been recently reported in Inconel 625 [15].

In spite of the fact that the precipitation sequence in Al–Mg–Cu alloys has been extensively studied using microscopy techniques, no work related with the elastic effects of precipitates in the bulk matrix and its correlation with mechanical behavior have been reported. In this way, X-ray diffraction peak broadening using the Rietveld method was used here to characterize the ageing behavior of Al–Mg–Cu alloys following microdeformation of the Al matrix due to coherency with the precipitates. The microstructural evolution has been correlated with the microhardness response of the alloy.

2. Experimental

The investigation was carried out on ternary alloys having the following chemical composition (wt.%):

Alloys	Al	Mg	Cu	Si	Fe	Mn	Cr	Ti	V
AMC	Bal.	4.28	0.68	0.047	0.052	0.0082	<0.001	<0.002	0.0041

A mixture of Al, Mg, and Cu was melted into a graphite crucible in an induction furnace under an Ar atmosphere. After homogenization, the cast ingots were rolled. The rolling process was divided in two steps: 1) Hot rolling of ingots from 24 mm to 9 mm at 400 °C and 2.5 m/min. 2) Cold rolling of 9 mm ingots to obtain 1 mm thick sheets. The sheets were cut using a SiC metallographic disc, into 10 mm × 20 mm specimens. Solution treatment was performed in a salt bath for 0.5 h at 550 °C and followed by water cooling at room temperature (≈20 °C). The ageing treatment was performed in a salt bath at 180 °C for several ageing times (from minutes to weeks) and followed by water quenching.

A Shimadzu HMV-2 microhardness tester was employed in order to obtain Vickers microhardness measurements. Microhardness samples were prepared by a standard metallographic process. The load retained was 490.3 mN (HV 0.05) for 10 s using a 40X objective lens. Mean values were obtained after 10 measurements per specimen.

The X-ray diffraction (XRD) profiles of the sample were recorded using a Bruker AXS model D8 Advanced diffractometer with CuKα radiation and a graphite monochromator. The scan was made between the angular range of 20°–120°. The step size and step time were 0.02° and 0.9 s per step, respectively, with the X-ray generator power set at 35 kV and 30 mA. Both the Rietveld refinement and profile analysis were made using Fullprof software. The instrumental broadening was estimated using a LaB_6 specimen. For the lattice parameter determination, Si polycrystalline powder was used as an internal standard.

The *attenuation factor* 2M fitting process was carried out employing a Matlab owner-routine. A non-linear Levenberg–Marquardt method was used to search for the best fit. The integral intensities were modeled with three pseudo-Voigt functions. Each function describes the matrix scattering in terms of 3 components: Bragg peak (B), static diffuse (SD) and quasilines peak (Q).

2.1. Method of Analysis

From XRD analysis, the crystal structure is determined from the intensities and the angular position of the Bragg peaks in the diffraction pattern. The microstructural information is deduced from the broadening of the Bragg peaks. The total broadening of the diffraction peaks is due to the instrumental broadening of the diffractometer and to the broadening due to average domain sizes (crystallite-size) and the lattice microstrains.

Among the different methods for analyzing the peak profile, the Rietveld method has been widely employed for this purpose. In this method, the whole diffraction profile is fitted by the Voigt approximation, the FWHM of the Gauss and Cauchy profile of the Voigt function is calculated from the pseudo-Voigt approximation parameters and the Thompson-Cox-Hastings formulation [16]. The intrinsic integral breadth is calculated from the β_G and β_C, intrinsic components for Gauss and Cauchy functions, respectively, using the DeKeijser formula [17]:

$$y = \frac{\beta_C}{\sqrt{\pi}\beta_G} \tag{1}$$

$$\beta^* = \frac{\beta_G}{-\frac{1}{2}y\sqrt{\pi} + \frac{1}{2}(\pi y^2 + 4)^{1/2} - 0.234ye^{(-2.176y)}} \left(\frac{\pi}{180}\right)\left(\frac{\mathrm{Cos}\theta}{\lambda}\right) \tag{2}$$

2.2. Integral Breadth Method

In the simplified integral breadth method the broadened peak due to the crystallite size and the lattice strain is assumed to be either a Cauchy function or a Gaussian function[18].This