Precipitation of Guinier-Preston Zones in Aluminum-Magnesium; A Calorimetric Analysis of Liquid-Quenched and Solid-Quenched Alloys

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A calorimetric analysis of precipitation in liquid-quenched (LQ; rapidly solidified) and solid-quenched (SQ; quenched after solution heat treatment) AlMg alloys was made. Nonisothermal annealing (constant heating rate) experiments (differential scanning calorimetry) were performed using specimens of various compositions (12 to 17 at. pct Mg) aged at fixed temperatures (293 to 353 K) during variable times (up to 3 years). Constraints to be imposed on the heating rates to be applied were discussed. Attention was paid in particular to the formation on aging and dissolution on subsequent annealing of Guinier-Preston (GP) zones. Quantitative analysis of the heat of dissolution of GP-zones led to estimates for the GP-zone solvus and the enthalpy of formation of GP-zones. The kinetics of formation and dissolution of GP-zones can be interpreted in terms of nucleation and excess-vacancy enhanced diffusion of magnesium. Rates of formation and dissolution of GP-zones are higher for SQ-alloys than for LQ-alloys, which is caused by a higher amount of excess vacancies retained after drastic SQ as compared to LQ by melt spinning where cooling in the last part of the quench can be relatively slow. The activation energy of GP-zone dissolution is generally smaller than that of GP-zone formation, which is interpreted in terms of a precipitation model where vacancy voids/loops, formed during quenching and/or in the beginning of aging, become unstable at temperatures where the GP-zones dissolve. As compared to the precipitation of GP-zones, the precipitation of $\beta'/\beta$ particles showed an "opposite" kinetic behavior: it starts earlier in the LQ-alloys than in the SQ-alloys, which is ascribed to heterogeneous nucleation at structural heterogeneities (as grain boundaries) present with a higher density in the LQ-alloys.

I. INTRODUCTION

Aging of an aluminum-rich matrix (face-centered cubic) supersaturated with dissolved magnesium, can ultimately lead to the precipitation of $\beta$ ($\text{Al}_3\text{Mg}_2$: face-centered cubic) particles (see phase diagram[10]). However, a number of metastable phases, which can occur before the emergence of the equilibrium phase ($\beta$), have been reported. There is general agreement concerning the occurrence of an intermediate $\beta'$ ($\text{Al}_3\text{Mg}_2$: hexagonal) phase immediately preceding the $\beta$ phase. But no consensus exists with respect to possible preprecipitates. Guinier-Preston (GP) zone formation can occur during aging at relatively low (e.g., room) temperature of AlMg alloys homogenized at elevated temperature and subsequently quenched (denoted as solid-quenched (SQ) alloys). Some authors report that at least about 10 at. pct Mg should be dissolved for GP-zone formation to occur at room temperature,[5] whereas others claim that this critical amount equals about 5 at. pct Mg.[4,5] Enhanced aging may lead to a more stable intermediate phase (as derived from a shift to a higher temperature of the endothermic DSC (Differential Scanning Calorimetry) peak ascribed to the GP-zone dissolution on nonisothermally heating (constant heating rate) an aged alloy). This phase has been interpreted as an ordered "GP-zone" (denoted as $\beta^{4(4)}$ or $\beta^{4(5)}$), possibly with an L1$_2$-type superstructure ($\text{Al}_3\text{Mg})\text{[6,7]}$

Only a few data exist about the aging of aluminum alloys prepared by rapid solidification from the liquid state (denoted as liquid-quenched (LQ) alloys). As compared to SQ alloys, in general one may expect that the initially high cooling/solidification rate for LQ alloys has large effects on the aging kinetics. This has been demonstrated by recent experiments with AlSi-alloys and was ascribed to a relatively high amount of excess vacancies and a very fine grain structure.[8] However, in some cases relatively low values have been reported for the excess-vacancy concentration after liquid-quenching[9] (see also results presented in this paper).

The purpose of this paper is to investigate by calorimetric analysis heat effects and kinetics of the formation and dissolution of preprecipitates in both LQ and SQ AlMg-alloys. Important stimuli for this work are the following: (i) the totally different precipitation behavior expected for LQ AlMg-alloys as compared to the previously investigated LQ AlSi-alloys[9] (no preprecipitates or intermediate phases have been reported for AlSi); (ii) the role of the type of quenching performed; in the only previous work known to us on precipitation in LQ AlMg alloys it was claimed that no GP-zone formation occurs.[10]

II. EXPERIMENTAL PROCEDURE

A. Preparation and Aging of Alloys

Liquid-quenched (LQ) AlMg-alloys containing 12.1, 12.8, 15.9, 16.1, and 17.2 at. pct Mg were prepared by melt-spinning (for details see Reference 12). Solid-
quenched (SQ) material was obtained by annealing meltspun ribbons in a hydrogen atmosphere (flow rate 40.7 cm/min) during 5 minutes at 723 K succeeded by quenching in ice water.

X-ray diffraction analysis (Debye-Scherrer photographs) demonstrated that all magnesium was in solid solution immediately after liquid or solid quenching; a second phase could not be detected.

Aging experiments were performed at room temperature and at temperatures up to 353 K in a thermostatically controlled oil bath (Tamson, type TC (V), temperature control within 1 K).

B. Calorimetry

After aging, the ribbons were cleaned with trichloroethylene and ethylalcohol. Thereafter they were chopped into small pieces. The calorimetric measurements were performed with a differential scanning calorimeter (Perkin-Elmer, DSC-2). Both the sample and the reference holder were made of graphite. A protective gas atmosphere of pure argon was employed.

For determination of the enthalpy changes in all the cases, a heating rate of 20 K/min was used (temperature range from 310 until 723 K = eutectic temperature of AlMg).

For determination of the activation energy of the dissolution of the GP-zones, the so-called Kissinger analysis was applied, using heating rates of 5, 10, 20, and 40 K/min (for a justification of the applicability of the Kissinger analysis to heterogeneous reactions in the solid state, see Reference 27).

Per sample two DSC-runs were successively performed; the second run was carried out in order to obtain the baseline.

III. CONSTRAINTS FOR THE HEATING RATE

Consider the schematic phase diagram presented in Figure 1(a). On aging at temperature $T_{\text{start}}$ an aluminum matrix initially supersaturated with magnesium (composition $x_0$), GP-zones develop. After a certain time of aging, $t$, the composition of the matrix has decreased and become $x_t$. By performing subsequently (nonisothermal) annealing experiments in a calorimeter (Differential Scanning Calorimetry) both the enthalpy change associated with and the kinetics of the dissolution of the GP-zones formed by aging at $T_{\text{start}}$ can be analyzed from the corresponding endothermic effect. Only for a limited range of heating rates reliable data can be obtained. During the anneal, with constant heating rate, a path in the phase diagram for the composition of the matrix can be indicated: the heating rate increases for the paths indicated in Figure 1(a) in the order 4-3-2-1.

A. Analysis of Enthalpy Change

If the decomposition process of the matrix on aging at $T_{\text{start}}$ has not been completed, a (small) exothermal effect can occur in a subsequent anneal with a relatively low heating rate, as a consequence of continued GP-zone formation, before the large endothermic effect corresponding to GP-zone dissolution occurs (see path 4 and corresponding DSC-curve in Figures 1(a) and (b)). Hence, for the analysis of the enthalpy change of GP-zone dissolution, the heating rate should be at least as large as that corresponding to path 3 in Figure 1(a): vertical path for $T < T_{\text{GP}}(x_t)$, thus avoiding GP-zone formation on annealing. This minimal heating rate is the smaller, the smaller $x_t$ (because the driving force for GP-zone formation decreases on continued aging).

For heating rates larger than or equal to the minimal one, the start temperature of the endothermic peak is equal to or larger than $T_{\text{GP}}(x_t)$. The minimal heating rate required for a vertical path in the phase diagram below the GP solvus ($x = x_t; T < T_{\text{GP}}(x_t)$) may be that large that for $T > T_{\text{GP}}(x_t)$ the path followed does not necessarily coincide with the GP-solvus, but it could be located above it. Hence, the end temperature of the endothermic peak for the minimal heating rate can be equal to or larger than $T_{\text{GP}}(x_t)$.

For heating rates smaller than or equal to that corresponding to path 3, such that the GP-solvus is followed at least for the late stages of GP-zone dissolution, the end temperature in the DSC-curve for the GP-zone dissolution peak equals the GP-solvus temperature corresponding to the gross content $x_0$ ($T_{\text{GP}}(x_0)$; Figures 1(a) and (b)).

B. Analysis of the Activation Energy

In order to analyze the (Arrhenius) kinetics of the GP-zone dissolution process, the heating rate should be that large that this dissolution process is governed by the atomic mobility; at least, the matrix composition should not follow the GP-zone solvus (see also References 14 and 15).

For heating rates smaller than or equal to that of path 3 the rate of GP-zone dissolution can be determined by the course of the matrix composition along the GP-solvus; the rate of GP-zone dissolution then is governed by the slope of the GP-zone solvus.

For heating rates well above that of path 3 (see paths 2 and 1 in Figure 1(a)) atomic mobility can be rate limiting for the dissolution. Then the DSC-peak signal shifts to higher