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Hardening of Al–Mg–Si alloys: Effect of trace elements and prolonged natural aging

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ABSTRACT

This study first provides a concise review of natural aging in Al–Mg–Si alloys and its effect on artificial aging. The second part investigates prolonged natural aging at different temperatures for >500 days of commercial and trace element added alloys. Together, the two parts improve the picture of underlying mechanisms and refine suggestions regarding the five stages of natural aging. Trace Sn- or Sn + In-added alloys show a trend towards higher activation energies of clustering, and a higher temperature dependency of natural aging than commercial alloys. This is attributed to an additional contribution of a thermally activated vacancy release from Sn- and In-vacancy pairs. Sn and In additions are suggested to decrease cluster number density while increasing cluster size. Prolonged natural aging increasingly retards artificial aging kinetics. This is interpreted according to increasingly slower cluster dissolution kinetics and slower preferential growth of β´´ needles. The reachable strength however seems to strongly depend on the ratio and size of coarse β´´ needles, preferentially grown, and the number of fine re-precipitated β´´ needles. Artificial aging after prolonged natural aging at 45 °C increases the artificial aging peak hardness due to a lower density of larger clusters than at lower temperatures.

1. Introduction

Although age-hardenable Al–Mg–Si alloys (6xxx series) were developed in the 1920s, the exact mechanisms controlling natural aging (n.a.) and the latter's effect on artificial aging (a.a.) are still not fully understood. The following presents a concise review of the most unclear phenomena. The description shows that n.a. clustering processes occur in distinct temporal stages that are associated with characteristic alloy behavior, but also that the duration and kinetics of these stages depend on chemical composition and heat treatment history. Together with a comparison to findings regarding Al–Mg and Al–Si alloys and an analysis of clustering theories based on solute-vacancy interaction, we suggest a refined overall mechanistic picture of n.a. Our in-depth analysis of recent literature and the connections we have drawn enable us to better understand the effect of n.a. temperature and prolonged storage on Al–Mg–Si alloys with and without trace element additions.

1.1. Natural aging in 6xxx series alloys

1.1.1. Five stages of clustering

Fig. 1 summarizes schematically the five stages of n.a. clustering introduced by Banhart et al. [1,2]. Most of the mechanisms suggested were derived from hardness, electrical resistivity (ρ), differential scanning calorimetry (DSC) and positron annihilation data (PALS).

The initial average positron lifetime τ_{av} decrease after quenching from solution treatment temperature (s.t.t.) is attributed to the first clustering stage 0 and the predominant annihilation of positrons in vacancy-related defects, i.e. quenched-in excess vacancies ($\square_{ex}$) or solute-vacancy complexes [3]. The decrease is faster and ends at a lower τ_{av} the higher the Mg content, and can be observed only in alloys of limited Mg content <0.6 at.% [1]. The subsequent short stage I is characterized by a nearly constant τ_{av}, which is pronounced only for alloys with a Mg/Si ratio close to 1. These alloys alone also show a small DSC clustering peak C0 in stage I as seen in Fig. 1 [1,4]. In stage I an initial (low) logarithmic electrical resistivity increase ρ and hardness increase are followed by a fast increase in stage II. The decomposition of the τ_{av} into positron lifetimes at defined locations τ_i shows that shortly after quenching 80–85% of the positron signal accounts for vacancy-related defects and the remainder for vacancy-free solute clusters [3]. This suggests that solute clustering sets in even during quenching. In stage II the τ_{av} decreases to a minimum as the signal for vacancy-free solute clusters

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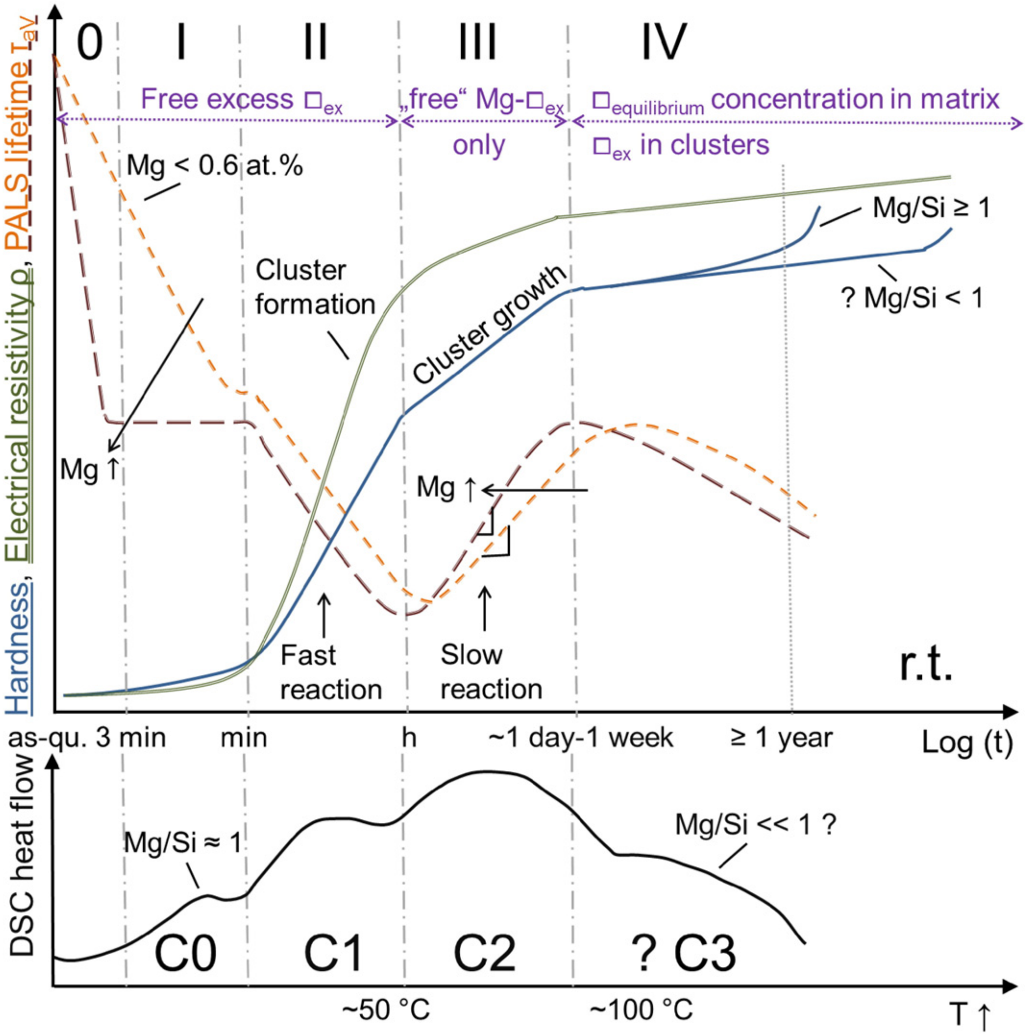

Fig. 1. Schematic representation of the five stages of natural aging (n.a.) clustering and suggestions regarding the mechanisms involved. Comparison of hardness, electrical resistivity ρ and average positron lifetime τ_{av} evolution at room temperature (r.t.) to differential scanning calorimetry (DSC) results. Note that cluster peaks obtained by linear heating reflect the same clusters formed with increasing n.a. time. Partly reproduced from ref. [1].

with lower lifetime increases up to ~70% [3]. The increasing number of vacancy-free solute clusters generates the clustering reaction C1 in DSC (Fig. 1), which we interpret as predominantly involving Si [4]. We attribute the re-increase of the τ_{av} in stage III to continuous Mg-addition to pre-formed solute clusters [1]. Stage III involves an intermediate logarithmic electrical resistivity and hardness increase and the DSC clustering reaction C2 probably starting around the end of stage II [1]. With time, the τ_i of vacancy-related defects becomes inseparable, i.e. vacancy-free solute clusters dominate [3]. With increasing Mg-content the τ_{av} in stage III increases faster and the transition to stage IV, in which the τ_{av} drops again, occurs earlier. Stage IV is accompanied by another slow-down of the hardness and resistivity increase [1]. While for the Si-rich alloy in refs. [5,6] hardness hardly increases at all in 1.5 years, in other alloys a significant non-linear hardness increase is observed in stage IV [6,7] (Figs. 1 and 3a). Possible mechanisms here are a coarsening or ordering and zone formation on the part of cluster C2 [1].

Liang et al. [8] reported on three clustering peaks in an Si-rich alloy investigated by PALS in ref. [1]. As the clustering reaction C1 has already terminated after the end of stage II (see Fig. 1), cluster C1 is weakly observed during a subsequent DSC measurement. Cluster C2 is observable until the end of stage III [1]. After stage IV another peak is observed [8] which is interpreted here as a possible C3 peak only observable in Si-rich alloys with a Mg/Si ratio of $\ll 1$ [9]. DSC data analysis indicates that the clustering process C1 resembles "cluster formation", while C2 and C3 resemble "cluster growth" [8].

1.1.2. Influence of trace elements

The wish to control n.a. kinetics and the negative effect on a.a. is of major importance for the Al manufacturing industry. The positive effect of trace elements such as Sn and In on temporary suppression of n.a. is known for Al–Cu alloys [10,11], but only a few recent investigations address Al–Mg–Si alloys [12–16]. Our group recently presented a design strategy [17] which involves fine-tuning of the alloy composition with respect to the Mg, Si, Cu and trace element content. N.a. could be suppressed for >6 months while retaining a significant a.a. potential [17], which is explained by the strong trapping of quenched-in excess vacancies in stable Sn-vacancy pairs [12,14–16,18]. This suppresses the formation of clusters during n.a. that act as relative stable vacancy prisons and reduce the a.a. potential [19]. Achieving the maximum trace element effect requires the quenching in of the maximum concentration of dissolved Sn atoms, i.e. (i) a high s.t.t. for maximum Sn solubility, (ii) a Sn content > solubility limit and (iii) a controlled content of Mg and Si. The interpretation of the trace elements effect on n.a. hardening and kinetics is used in this paper to generate a better understanding of the processes underlying n.a.