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Design strategy for controlled natural aging in Al–Mg–Si alloys

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ABSTRACT

This study presents a design strategy for Al–Mg–Si alloys to control natural aging. Recently, trace addition of Sn was shown to suppress natural aging for up to two weeks, which was explained by the strong trapping of vacancies to Sn atoms. Here we explore the effect of solution treatment temperature, the combination of trace elements such as Sn and In, and the composition of main hardening elements Mg, Si and Cu on natural aging. The results are discussed based on the dissolvable amount of trace elements and their effect on diffusion retardation, and solute clustering mechanisms in Al–Mg–Si alloys. Thermodynamic calculations using the CALPHAD approach show that maximum retardation of natural aging is achievable at the highest trace element solubility, which exists at significantly different solution treatment temperatures for Sn or In. The effects of Mg, Si and Cu content on natural aging kinetics are interpreted via their influence on the Sn solubility and clustering mechanisms. It is proposed that Sn additions reduce the concentration of excess vacancies, which is most important for early Si clustering, and that the effect of Cu is comparable to the effect of Sn, but less pronounced. Based on the investigated parameter space, a design concept is proposed and an Al–Mg–Si alloy showing suppression of natural aging for >6 months and significant artificial aging potential is demonstrated.

1. Introduction

Age hardenable Al–Mg–Si alloys (6xxx-series) are widely used in the transport, automotive, shipbuilding, and aviation industry [1–3]. Aluminum allows lightweight construction for improved fuel efficiency and reduced CO_2-emissions. 6xxx-series alloys are especially attractive as they combine good formability with medium to high strength after age hardening, good corrosion resistance, and weldability. In the automotive industry, for example, they are used as outer skin alloys, for non-decorative inner parts, and structural or crash components with individual property criteria [1–5]. Yet, the ever-growing demand to increase formability and strength for more complex parts of lower weight drives the alloy development considerably [4–7].

The delivery of semi-finished products mostly occurs after quenching to enable forming operations at low strength prior to the final heat treatment to gain high strength [4,8–10]. During natural aging (n.a.), which starts directly after quenching from solution heat treatment, the material hardness increases due to solute clustering of Mg- and Si-atoms [11–15]. This generates two problems for the transportation industry: first, dynamic hardening during n.a. reduces formability [4]; second, clustering results in a negative effect of n.a. on subsequent artificial aging (a.a.) [12,13,16–18]. The transportation industry, however, requires several months of stable formability combined with good a.a. performance so as to obtain reproducibility of designs that have increasing complexity [4,10]. Hence, pre-aging treatments have been developed to improve a.a. and to achieve a relatively "stable" material state [8,10,19–22]. Pre-aging treatments, however, result in undesired hardness increase [10].

This study presents a novel design strategy for 6xxx-alloys to achieve maximal suppression of n.a. hardening after quenching

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while still achieving a potential for significant a.a. The study builds on recent research showing that trace tin (Sn) addition to the alloy AA6061 can suppress n.a. for 2 weeks and simultaneously improve the a.a. potential [23–26]. The mechanism behind this is to prevent excess vacancy-mediated diffusion during n.a. through permanent trapping of vacancies by trace elements, while facilitating such diffusion during a.a. through vacancy release from the thermally unstable trace element-vacancy complexes [23,24,26]. Here, detailed investigation of the effects of solution treatment temperature and Mg, Si and Cu content in alloys, with and without trace element additions, leads to a designed Al–Mg–Si alloy showing n.a. stability for more than 6 months.

2. Methods

Table 1 shows the alloys studied here. Alloys 1–13 were produced at the laboratory scale starting from AA6061 base alloys. After re-melting, pure Mg, Si, Cu, Sn or Sn + In were added to the base alloys to obtain the compositions listed in Table 1. Ar gas purging was applied to reduce the hydrogen content before the alloys were cast to slabs. After cutting and homogenization, hot rolling was conducted. To check the chemical composition of the final sheets, optical emission spectrometry and, for In, inductively coupled plasma mass spectroscopy, were used. Alloys 14 and 15 with and without Sn addition were industrially produced and supplied by AMAG rolling GmbH in the form of wrought plates. Note that all chemical compositions in Table 1 are near to commercial AA6061 alloys.

Solution heat treatment of hardness test samples was performed in a circulating air furnace (Nabertherm N60/85 SHA) at temperatures between 510 and 570 °C for 1.2×10^3 s. Subsequent quenching was carried out in water at room temperature and, for n.a., samples were kept in a Peltier-cooled incubator IPP (Memmert) at 25 °C. Artificial aging was undertaken in an oil bath.

Brinell hardness measurements (HBW 2.5/62.5) were carried out using an EMCO-Test M4 unit. A maximum standard deviation of 2.0 HBW was achieved.

Thermodynamic calculations of the alloys were performed using FactSage™ 6.4 software [27,28] together with the FACT FTlite light alloy database (2014). For the equilibrium calculations the alloy compositions according to Table 1 were entered and all possible phases selected from the databases. Data of phases and their stabilities, compositions and element solubility were calculated between 320 °C and 600 °C. Table 2 shows the calculated Mg, Si and Cu solubility at the solution treatment temperatures 530 °C and 570 °C. Stable Si containing Fe and Ti phases [29–32] reduce the quenchable Si solubility.

Table 2
Calculated solubility of alloying elements at solution treatment temperatures (s.t.t.) 530 °C and 570 °C.

Solubility at s.t.t.		530 °C			570 °C		
Alloy	Symbol MgSiCu	Mg [wt.%]	Si [wt.%]	Cu [wt.%]	Mg [wt.%]	Si [wt.%]	Cu [wt.%]
1	↓↓↓	0.73	0.30	0.24	0.79	0.32	0.23
2	↓↓↓	0.77	0.36	0.22	0.79	0.39	0.21
3	↓↓↓	0.79	0.29	0.22	0.79	0.29	0.22
4	↓↓↓	0.82	0.34	0.22	0.82	0.36	0.22
5	~~~	0.75	0.40	0.31	0.87	0.48	0.30
6	↑~~	0.79	0.38	0.30	0.96	0.48	0.29
7	↓~~	0.70	0.45	0.30	0.77	0.50	0.30
8	~↑~	0.69	0.51	0.29	0.85	0.59	0.29
9	~↓~	0.80	0.35	0.25	0.87	0.40	0.25
10	~~↑	0.74	0.41	0.39	0.84	0.48	0.38
11	~~↓	0.74	0.43	0.21	0.86	0.51	0.21
12	↓↓↓	0.77	0.37	0.22	0.78	0.39	0.21
13	~~~	0.74	0.42	0.25	0.83	0.48	0.24
14	**↓↓↑**	0.78	0.21	0.36	0.79	0.24	0.36
15	**↓↓↑**	0.77	0.22	0.36	0.77	0.26	0.36

The designed alloy 14 shows very low Si (indicated by the arrow in bold).

3. Results

3.1. Influence of solution treatment temperature

Figs. 1 and 2 show the effect of solution treatment temperature on n.a. kinetics of alloys 1–3 containing 430, 96 and 70 at. ppm Sn, respectively, and alloy 4 (Table 1). Alloy 4 represents the "Sn-free" reference alloy with low Mg, Si and Cu content (↓: low, symbol: ↓↓↓) and commercial amounts of Sn and impurity elements (compare ref. [23]) for industry-orientated comparisons. A solution heat treatment at 570 °C is compared to 550 °C, 530 °C and 510 °C. After annealing at 570 °C, the alloys containing 430 and 96 at. ppm Sn preserve the as-quenched hardness for ~14 days (Fig. 1a). The alloy with 70 at. ppm Sn starts hardening after more than 4 days (Fig. 1b). At lower solution treatment temperatures hardening

Table 1
Measured composition of alloys (Al in balance).

Alloy	Symbol MgSiCu	Sn [at. ppm]	Sn [wt.%]	In [wt.%]	Mg [wt.%]	Si [wt.%]	Cu [wt.%]	Fe [wt.%]	Mn [wt.%]	Cr [wt.%]	Zn [wt.%]	Ti [wt.%]
1	↓↓↓	430	0.188		0.82	0.63	0.23	0.59	0.111	0.147	0.059	0.079
2	↓↓↓	96	0.042		0.78	0.61	0.21	0.49	0.119	0.154	0.045	0.040
3	↓↓↓	70	0.030		0.79	0.58	0.21	0.48	0.110	0.147	0.057	0.088
4	↓↓↓	6	0.0026		0.81	0.62	0.22	0.49	0.111	0.146	0.059	0.081
5	~~~	94	0.041		0.87	0.72	0.30	0.51	0.118	0.148	0.045	0.041
6	↑~~	94	0.041		0.96	0.71	0.29	0.46	0.116	0.147	0.044	0.043
7	↓~~	96	0.042		0.77	0.73	0.30	0.46	0.117	0.148	0.045	0.042
8	~↑~	91	0.040		0.85	0.83	0.29	0.45	0.116	0.147	0.045	0.043
9	~↓~	94	0.041		0.86	0.61	0.25	0.46	0.116	0.148	0.045	0.042
10	~~↑	91	0.040		0.84	0.70	0.38	0.44	0.115	0.150	0.043	0.043
11	~~↓	89	0.039		0.86	0.74	0.20	0.48	0.116	0.151	0.045	0.044
12	↓↓↓	98	0.043	0.039	0.78	0.62	0.21	0.50	0.118	0.152	0.045	0.039
13	~~~	91	0.040	0.040	0.84	0.71	0.25	0.45	0.115	0.150	0.043	0.044
14	**↓↓↑**	96	0.042		0.78	0.43	0.36	0.46	0.109	0.136	0.047	0.056
15	**↓↓↑**	5	0.002		0.76	0.41	0.36	0.45	0.109	0.138	0.045	0.053

Alloy 14 shows a very low Si content (indicated by the arrow in bold).