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**ALUMINUM ALLOYS:
DEVELOPMENT,
CHARACTERIZATION
AND APPLICATIONS**

Casting and Solidification

SESSION CHAIR

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STATISTICAL AND THERMODYNAMIC OPTIMIZATION OF TRACE-ELEMENT MODIFIED Al-Mg-Si-Cu ALLOYS

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Abstract

Al-Mg-Si-Cu alloys exhibit natural aging, which negatively influences artificial aging. Additions of trace elements have been recently shown to eliminate this effect: At room temperature quenched-in vacancies are trapped by trace solutes in the ppm range and natural aging is suppressed, while at higher temperatures these vacancies are released and artificial aging is promoted. In this study we determine an optimum in chemical composition and solution heat treatment temperature for Sn and In-doped Al-Mg-Si-Cu alloys. Automated thermodynamic calculations coupled with a statistical evaluation of influencing parameters on solubility of Mg, Si, Cu, Sn and In were used to find maximum strengthening potential and dissolved trace element content. Theoretical predictions are compared to aging experiments. The method enables detailed and rapid analysis of a wide compositional and temperature space in multicomponent systems.

Introduction

Al-Mg-Si-Cu alloys are an important class of aluminum alloys for applications such as construction, automotive engineering, shipbuilding, and aircraft engineering [1]. In most cases Al-Mg-Si-Cu alloys obtain their strength from precipitates formed during artificial aging at 150 °C to 180 °C after quenching [2]. A number of different precipitates have been observed to form during artificial aging. Their nature in terms of structure and chemical composition as well as their transformation path in various types of Al-Mg-Si-Cu alloys is rather complex. Figure 1 shows a summary of the possible precipitates evolving during aging at temperatures above room temperature (RT).

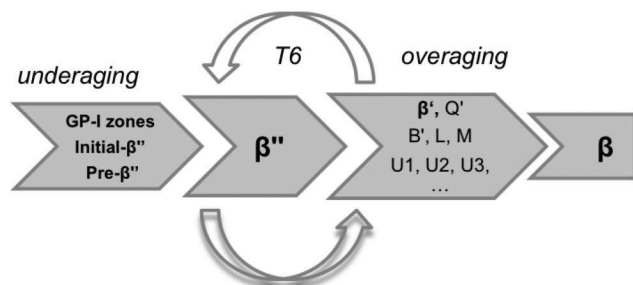


Figure 1. Possible precipitates evolving during artificial aging in Al-Mg-Si-Cu alloys [3, 4]

It has been claimed that there is an invariant arrangement of Si nanopillars in particles formed during aging [5], but it is not clear yet if this is valid for the whole group of Al-Mg-Si-Cu alloys [6]. In general, GP-I zones with a size of 1 to 3 nm are the earliest

stages, which can be observed upon aging at elevated temperatures [7, 8]. Note that these zones are also called Mg₂Si-clusters [9] or clusters [10] by some authors. β'' needles [8, 11] are the most frequently observed precipitates in peak aged conditions (T6) in alloys without or low amounts of Cu [12]. Various lath-, needle- or rod-shaped phases have been reported for overaged conditions [3, 4] although some of those phases can also occur in peak-aged conditions (this is indicated by the arrows in Figure 1). This behavior depends on the chemical composition and the individual processing route. For example β' and B' have been shown to form instead of β'' if AA6060 is deformed before aging [13]. Furthermore, the Cu content is known to effect the type of precipitate formed [4]. A high Cu-content favors the formation of Q' [3, 12]. However, the rod-shaped phase β' [14] is the most commonly found type in overaged conditions. The phase β represents the equilibrium Mg₂Si phase [3].

Although precipitation during artificial aging in Al-Mg-Si-Cu alloys is complex and not fully understood, processes that occur after quenching at RT (natural aging) are even less resolved. Yet, the topic is of special interest since natural aging is known to reduce artificial aging kinetics by an order of magnitude and also the achievable strength in high-strength Al-Mg-Si-Cu alloys [15]. This effect appears quickly after quenching [16, 17], but is largely unavoidable as there are several constraints in the industrial production and application of these alloys:

- Technological (necessary manipulation time after quenching, e.g. for forming operations or for stretching to reduce internal stresses)
- Physical (due to finite values of the heat transfer coefficient and the thermal conductivity to heat large parts to artificial aging temperature)
- Logistical (transport of the quenched material from the alloy producer to the customer where forming operations and artificial aging are performed)

In Ref. [18] we suggested a mechanism that clusters formed during natural aging act as prisons for excess-vacancies during artificial aging and therefore retard the nucleation of precipitates. Although, this is a simple theoretic conjecture, it has already been used successfully to present a solution to the problem of natural aging by manipulation of the excess-vacancy mobility [19]. Through the addition of trace amounts of solutes with high attractive binding energy to vacancies excess-vacancies are trapped at RT, which retards the formation of the detrimental clusters. During subsequent artificial aging the trapped excess-vacancies are released and enable excess-vacancy assisted fast nucleation of the strengthening precipitates.

The trapping efficiency of solutes was shown to depend on their concentration in solid solution and their binding energy to

vacancies [19]. For Sn as one possible trace element we recently found that its maximum dissolved amount in Al-Mg-Si-Cu strongly depends on the solution treatment temperature and the composition of the actual alloy [20].

In this study we present a method to develop Al-Mg-Si-Cu alloys with high potential for precipitation strengthening and a maximized concentration of dissolved trace element concentration. In addition, we explore the possibility to combine different types of trace elements. An automated thermodynamic calculation routine coupled with a statistical evaluation of solubility data is presented as a method for rapid analysis of a wide compositional and temperature space in multicomponent systems. The theoretical predictions are validated via natural aging experiments.

Methods

The compositional parameter space to maximize the content of solutes responsible for precipitation and the concentration of trace elements upon a solution heat treatment between 530 °C and 570 °C was studied in accordance to Table I.

Table I. Compositional ranges (in wt.%)

Element	Range
Si	0.3 – 1.5
Fe	0 – 0.8
Cu	0 – 1.5
Mn	0 – 0.5
Mg	0.3 – 1.5
Cr	0 – 0.5
Zn	0 – 0.5
Ti	0 – 0.2
Sn	0.015 – 0.10
In	0.015 – 0.05
Al	Bal.

Design of experiments (DoE) was used to generate parameter combinations (software used: MODDE™ 7.0) from Table I. Individual sets of compositions and temperatures were then read by macro processing to FactSage™ 6.4 software [21]. FACT FTlite light alloy database (2013) was applied to perform thermodynamic calculations of the solubility of Mg, Si, Cu, Sn, and In in FCC aluminum according to the Calphad approach. Calculated solubility data were then used to create regression models to allow a quick and easy identification of most important parameters (composition, temperature) on solubility. More than 6000 equilibrium calculations have been performed to explore the wide compositional and temperature space.

Table I. Composition of the model alloys (in wt.%)

Alloy / Element	A1	A2	A3	B1	B2	B3
Si	1.00	1.01	1.01	0.83	0.84	0.82
Fe	0.28	0.28	0.28	0.26	0.28	0.26
Cu	0.58	0.59	0.59	0.58	0.59	0.57
Mn	0.21	0.21	0.21	0.21	0.22	0.21
Mg	0.29	0.29	0.29	1.16	1.16	1.14
Cr	-	-	-	-	-	-
Zn	0.02	0.02	0.02	0.01	0.01	0.01
Ti	0.02	0.03	0.02	0.02	0.02	0.02
Sn	-	0.05	0.05	-	-	0.05
In	-	-	0.03	-	0.03	0.03
Al	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.

Model alloys to support the theoretical predictions were produced experimentally according to the compositions given in Table I. Chemical composition was determined by optical emission spectrometry.

Solution heat treatment of the alloys was performed in a circulating air furnace at 530 °C for 20 min. Specimens were then quenched in water at RT, followed by natural aging at 25 °C in a peltier-cooled incubator.

Brinell hardness measurements (HBW 2.5/62.5) were performed in order to follow natural aging.

Results and Discussion

Computational evaluation of trace element additions

Exploration of the effects of the elements given in Table I on the thermodynamic solute super-saturation of trace elements was performed by a multi-linear regression using a partial least squares algorithm. Figures 2, 4 and 5 show the effects of the compositional parameters listed in Table I on the Sn or In solubility at 530 °C, 550 °C and 570 °C. A 95 % confidence interval for the model is given. Statistical parameters such as R^2 (explains how well the model fits the data) and Q^2 (explains how well the model predicts new data) are also given and were found to be excellent. The effects display the change in the Sn or In solute super-saturation when an element is varied from the low level to the high level (Table I) and all other elements are kept at their averages. For an interaction effect, the effect of one element depends on the amount of another element. The interaction effect represents a synergy or an antagonism of two elements on the Sn or In solubility.

For an alloy formed from Al, Mg, Si, Cu, Fe, Mn, Cr, Ti, Zn and Sn, the achievable amount of Sn in solid solution depends on the following linear effects of the alloying elements: Addition of Mg, Si, Cu or Zn (descending order) decreases the solubility of Sn. Higher amounts of Fe, Ti and Mn (descending order) increase the solubility of Sn. However, these are indirect effects, since the elements form intermetallic phases with Si and therefore reduce the Si content. Furthermore, the interaction effects Si*Mg, Cu*Mg decrease the negative effect of the individual elements on the Sn solubility (e.g. if Mg and Si are both high, this shows up to be not so dramatic as expected from the individual effects). An increase of the solution temperature decreases the negative influence of Mg and Si. However, the negative effect of Cu strongly increases with increasing temperature, because Cu-addition decreases the solidus temperature of the alloy.

Detailed modeling of the reduced system Al-Mg-Si-Cu-Sn without Fe, Mn, Ti, Zn and Cr, but including the temperature between 530 °C to 570 °C was used to optimize the solubility of Sn with regard to a high content of Mg, Si, and Cu. Figure 3 shows contour plots of the major compositional influences on Sn solubility at (a) 570 °C and (b) 530 °C solution treatment temperature. Labels at the contour lines indicate the Sn content in solid solution. Obviously, high Sn solubility can be reached at high temperature and low Mg and Si content (Figure 3a). However, no Cu can be added at 570 °C, because Cu strongly reduces the Sn content due to partial melting. A similar high solubility of Sn is predicted at lower temperature (Figure 2b), but enabling a higher Si content and also a much higher content of Cu, which also leads to a higher solute super-saturation of elements which promote precipitation strengthening [22].

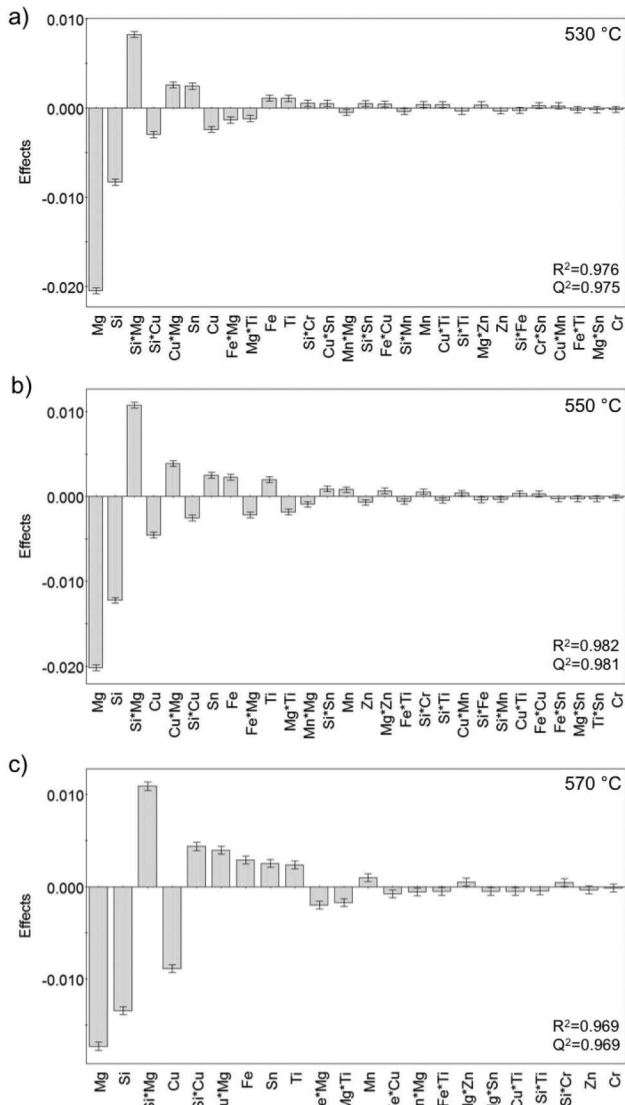


Figure 2. Effects of the alloying elements on the solute super-saturation of Sn at (a) 530 °C (b) 550 °C and (c) 570 °C

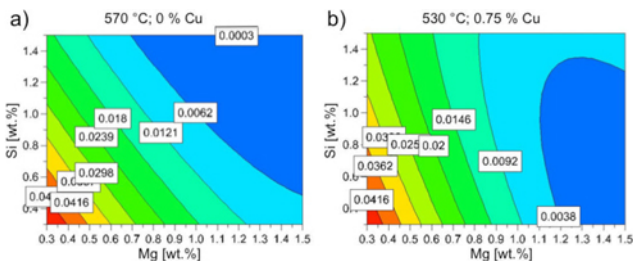


Figure 3. Contour plots of the major compositional influence on Sn solubility [wt.%] at (a) 570 °C and (b) 530 °C solution treatment temperature

Indium was also shown to exhibit a high attractive binding energy to vacancies [23]. Hence, like it was shown for Sn [19] also for In a positive aging effect can be assumed, providing that a sufficient amount of In can be dissolved in the aluminum matrix. An optimal situation with regard to a long suppression of clustering at RT, would be an combined effect from Sn and In. Figure 4 shows

the effects of the alloying elements on the solute super-saturation of Sn when In is present. Addition of Mg, Si, Cu or In decreases the solubility of Sn in descending order. Higher amounts of Fe, Ti and Mn (descending order) increase the solubility of Sn, which is again an indirect effect of the formation of intermetallic phases with Si. Furthermore, the interaction terms Si*Mg decrease the negative effect of the individual elements on the Sn solubility, also if In is present. An increase of the temperature decreases the negative influence of Mg and increases the negative effect of Cu.

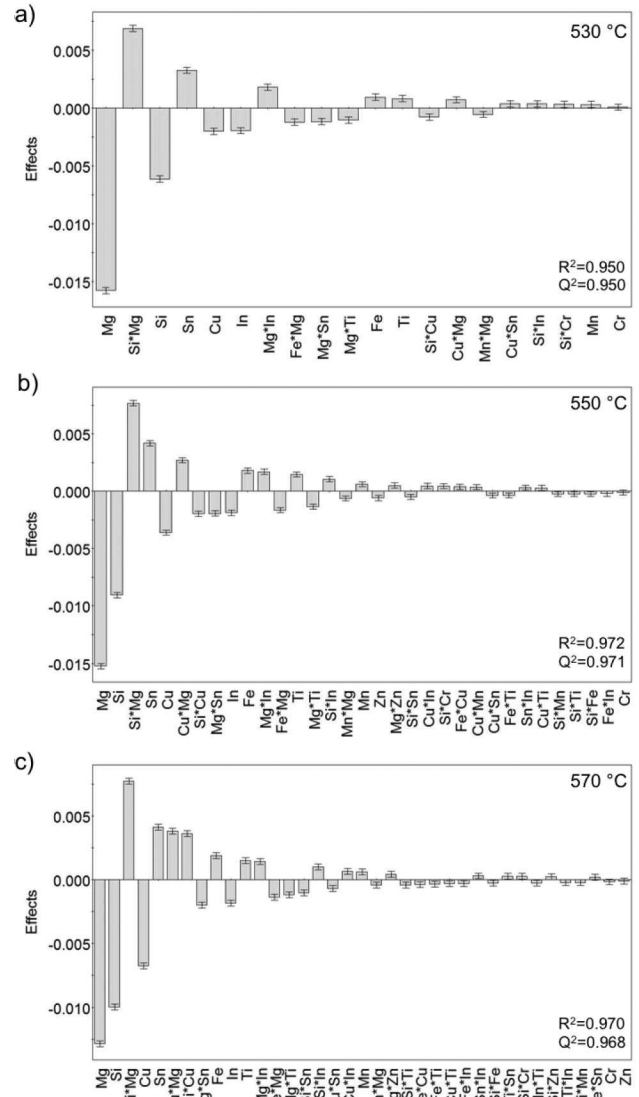
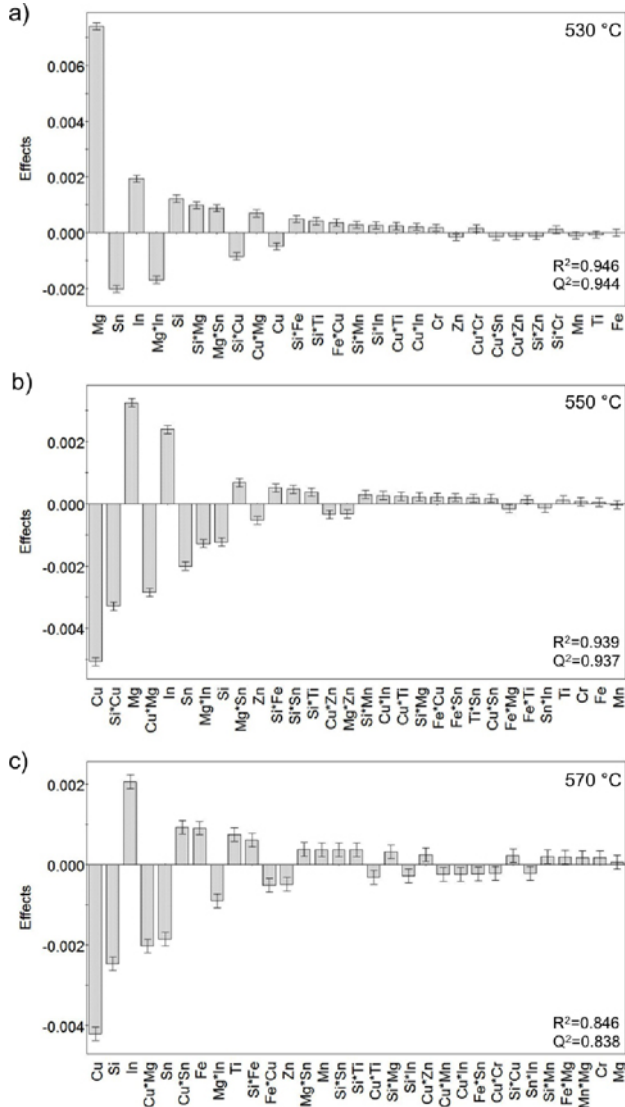


Figure 4. Effects of the alloying elements on the solute super-saturation of Sn at (a) 530 °C (b) 550 °C and (c) 570 °C when In is present

Figure 5 shows the effects of the alloying elements on the solute super-saturation of In when Sn is present. Contrary to the findings for Sn, additions of Mg and Cr increase the solubility of In (descending order). Higher amounts of Sn, Ti, Mn and Cu decrease the solubility of In in descending order. Si can be either positive or negative, depending on the temperature. At low temperature a higher amount of Si increases the In solubility while at high temperature Si reduces the In solubility. The positive

effect of Mg addition at low temperature also reduces with rising temperature. As observed for the Sn solubility, Cu shows a pronounced negative effect at high temperature due to partial melting.



Detailed modeling of the reduced system Al-Mg-Si-Cu-Sn-In in the temperature range between 530 °C to 570 °C revealed that an opposing trend exists for the achievable solubility of Sn and In. Figure 6 shows contour plots of the major compositional influences on the solubility of Sn and In at 530 °C. High In solubility can be reached at 530 °C with a high amount of Mg and a low amount of Sn (Figure 6a). Also Cu can be added at 530 °C to increase the potential for precipitation strengthening. However, the behavior of In is opposing a maximization of the Sn content in solid solution. High solubility of Sn can be reached at 530 °C with a low amount of Mg and a low amount of In (Figure 6b). Also in this case Cu can be added to increase the potential for precipitation strengthening. Nevertheless, a combination of Sn

and In to increase their total amount dissolved in aluminum seems not possible from a thermodynamic point of view.

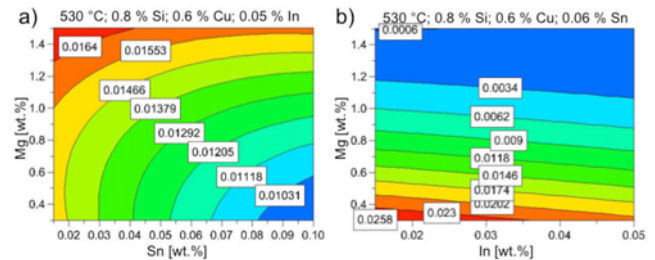


Figure 6. Contour plots of the major compositional influence on (a) In and (b) Sn solubility at 530 °C

Design of alloys and validation of predictions

In Ref. [22] a high nominal content of Mg, Si and Cu was generally shown to increase the amount of those elements in solid solution, if the solution treatment occurs about their solvus temperature and below the solidus temperature of the alloy. Furthermore, Fe and Ti are known to reduce the amount of Si dissolved in the aluminum matrix [22]. According to these aspects and the results from our parameter space investigation for the achievable amount of dissolved trace elements with high binding energy to vacancies, we designed the alloys shown in Table 1. Beside this, we considered some restrictions for industrial alloys (e.g. for the production from secondary raw material). All alloys are optimized for a solution treatment temperature of 530 °C. Alloy group A is designated to a maximized Sn solubility. Thus, a fairly small Mg content was chosen (see Figure 3). However, Cu was added to increase the potential for precipitation strengthening. Alloys B1 to B3 exhibit an optimized composition for high In solubility. In this alloy group the Mg content is high. Also here a high Cu content was chosen.

In addition to the development of a high strength alloy with retarded clustering during natural aging, the following questions were considered in choosing the alloy compositions: i) how trustful are the results from thermodynamic predictions for the solubility of trace elements in a wide parameter space and ii) is it possible to combine the effect of two trace elements with strong binding energy to vacancies?

Figure 7 shows hardness curves upon natural aging at 25 °C for all alloys after quenching from 530 °C. The addition of 0.06 wt.% Sn (above the predicted solubility limit) to alloy A1 retards hardening for approximately 2 weeks (alloy A2, Figure 7a). For an addition of 0.03 wt.% of In to A2 no combined effect of the two trace elements is perceived, i.e. alloy A3 also starts hardening after 2 weeks at 25 °C. This finding is perfectly supported by our findings in Figures 5 and 6. If the system is optimized for Sn and Sn is present, In can hardly be dissolved in aluminum.

Figure 7b shows natural aging results for the alloys optimized for the addition of In. The addition of 0.03 wt. % In (above the predicted solubility limit) to the alloy B1 retards the hardening only for 1 day (alloy B2, Figure 7b). Again, a combined effect due to Sn and In is not achievable. B2 shows nearly the same behavior as the alloy B3 containing both elements B3.

Comparing groups A and B also fits to the predictions made in the previous section. It was reported that the amount of dissolved trace elements influences the suppression of hardening [19]. The dissolvable amount of In is predicted to be lower than that of Sn (see Figure 6). Furthermore the binding energy of In to vacancies is around 25 % lower than the binding energy of Sn [23].

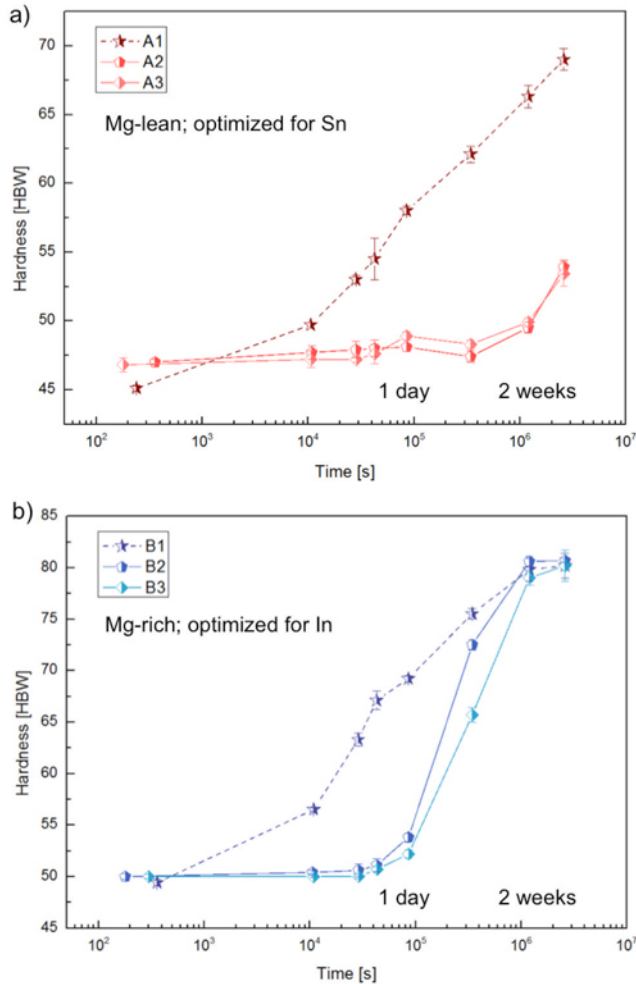


Figure 7. Hardness curve upon natural aging for (a) alloys A1, A2, A3 and (b) B1, B2, B3

Conclusions

We showed a method to develop alloys with high potential for precipitation strengthening and maximized solubility of trace elements to modify clustering.

- A high solute super-saturation of Sn in Al-Mg-Si-Cu alloys can be reached at low Mg content, while a high solubility of In requires a high Mg content.
- A combined effect of Sn and In is not achievable, also because the presence of Sn strongly decreases the solubility of In.
- Cu addition can be used to increase the precipitation strengthening potential without significantly affecting the solubility of trace elements. However, the solution treatment temperature has to be low enough to avoid partial melting.
- Thermodynamic calculations showed good predicative power for the solubility of trace elements confirmed by natural aging experiments.

In general, automated thermodynamic calculations coupled with a statistical evaluation of the output data are shown to be a quick method for efficient alloy development.

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References

1. C. Kammer, *Aluminium handbook* (Berlin: Beuth; 2011).
2. R.S. Archer, Z. Jeffries, "New Developments in High-strength Aluminum Alloys," *Trans AIME* 71 (1925), 828-863.
3. C. Ravi, C. Wolverton, "First-principles study of crystal structure and stability of Al-Mg-Si-(Cu) precipitates," *Acta Mater* 52 (2004), 4213-4227.
4. D.J. Chakrabarti, D.E. Laughlin, "Phase relations and precipitation in Al-Mg-Si alloys with Cu additions," *Prog Mater Sci* 49 (2004), 389-410.
5. J.H. Chen, E. Costan, M.A. van Huis, Q. Xu, H.W. Zandbergen, "Atomic pillar-based nanoprecipitates strengthen AlMgSi alloys," *Science* 312 (2006) 416-419.
6. H.K. Hastings, A.G. Frøseth, S.J. Andersen, R. Vissers, J.C. Walmsley, C.D. Marioara, et al., "Composition of β'' precipitates in Al-Mg-Si alloys by atom probe tomography and first principles calculations," *J Appl Phys* 106 (2009), 123527.
7. J. Buha, R.N. Lumley, A.G. Crosky, K. Hono, "Secondary precipitation in an Al-Mg-Si-Cu alloy," *Acta Mater* 55 (2007), 3015-3024.
8. J.J. Andersen, H.W. Zandbergen, J.E. Jansen, C. Taeholt, U. Tundal, O. Reiso, "The crystal structure of the β'' phase in Al-Mg-Si alloys," *Acta Mater* 46 (1998), 3283-3298.
9. F. De Geuser, W. Lefebvre, D. Blavette, "3D atom probe study of solute atoms clustering during natural ageing and pre-ageing of an Al-Mg-Si alloy," *Phil Mag Lett* 86 (2006), 227-234.
10. A. Serizawa, S. Hirose, T. Sato, "3DAP Characterisation and Thermal Stability of Nano-Scaled Clusters in Al-Mg-Si Alloys," *Mater Sci Forum* 519-521 (2006), 245-250.
11. H.W. Zandbergen, S.J. Andersen, J. Jansen, "Structure determination of Mg₅Si₆ particles in Al by dynamic electron diffraction studies," *Science* 277 (1997), 1221-1225.
12. G.A. Edwards, K. Stiller, G.L. Dunlop, M.J. Couper, "The precipitation sequence in Al-Mg-Si alloys" *Acta Mater* 46 (1998), 3893-3904.
13. K. Teichmann, C.D. Marioara, S.J. Andersen, K.O. Pedersen, S. Gulbrandsen-Dahl, M. Kolar, et al., "HRTEM study of the effect of deformation on the early precipitation behaviour in an AA6060 Al-Mg-Si alloy," *Phil Mag* 91 (2011), 3744-3754.
14. R. Vissers, M.A. van Huis, J. Jansen, H.W. Zandbergen, C.D. Marioara, S.J. Andersen, "The crystal structure of the β' phase in Al-Mg-Si alloys," *Acta Mater* 55 (2007), 3815-3823.
15. P. Brenner, H. Kostron, "Über die Vergütung der Aluminium-Magnesium-Silizium-Legierungen (Pantal)," *Z Metallkd* 4 (1939), 89-97.

16. I. Kovačs, E. Nagy, J. Lendvai, "Mechanism of Clustering in Supersaturated Solid-Solutions of Al-Mg₂Si Alloys," *Acta Metall Mater* 20 (1972), 975-983.
17. J. Banhart, C.S.T. Chang, Z.Q. Liang, N. Wanderka, M.D.H. Lay, A.J. Hill, "Natural Aging in Al-Mg-Si Alloys - A Process of Unexpected Complexity," *Adv Eng Mater* 12 (2010), 559-571.
18. S. Pogatscher, H. Antrekowitsch, H. Leitner, T. Ebner, P.J. Uggowitzer, "Mechanisms controlling the artificial aging of Al-Mg-Si Alloys," *Acta Mater* 59 (2011), 3352-3363.
19. S. Pogatscher, H. Antrekowitsch, M. Werinos, F. Moszner, S.S.A. Gerstl, M.F. Francis, et al., "Diffusion on Demand to Control Precipitation Aging: Application to Al-Mg-Si Alloys," *Phys Rev Lett* 112 (2014), 225701.
20. M. Werinos, H. Antrekowitsch, W. Fragner, T. Ebner, P.J. Uggowitzer, S. Pogatscher, "Influence of Sn-solubility on suppression of natural aging in an AA6061 aluminum alloy," MS&T '14. Pittsburgh, USA 2014.
21. C.W. Bale, P. Chartrand, S.A. Degterov, G. Eriksson, K. Hack, R. Ben Mahfoud, et al., "FactSage thermochemical software and databases," *Calphad* 26 (2002), 189-228.
22. S. Pogatscher, H. Antrekowitsch, P.J. Uggowitzer, "Interdependent effect of chemical composition and thermal history on artificial aging of AA6061," *Acta Mater* 60 (2012), 5545-5554.
23. C. Wolverton, "Solute-vacancy binding in aluminum," *Acta Mater* 55 (2007), 5867-5872.