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Stabilizing effect of alloying elements on metastable phases in cast aluminum alloys by CALPHAD calculations

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A B S T R A C T

Thermo-Calc software equipped with its TCAL4.0 database for aluminum alloys was used to investigate the influence of a number of alloying elements on the temperature stability of metastable phases such as θ'-Al_2Cu and β'-Mg_2Si. These phases are well-known to provide precipitation hardening thus increasing the mechanical properties of cast aluminum alloys for cylinder heads application. Two categories of elements are identified depending on their influence on the metastable phases stability: (i) destabilizing or non-stabilizing (Li, Hf, Cr and Ce) and (ii) stabilizing (V, Ti, Cr, and Sc). According to the thermodynamic calculations, Ti has the strongest stabilizing effect on θ'-Al_2Cu and β'-Mg_2Si as well as on their precursors. The computed predictions are compared with data obtained by DSC and the Ti effect on the temperature stability of metastable phases is confirmed experimentally.

1. Introduction

The EU is setting increasingly stringent regulations regarding emissions of internal combustion engines. This resulted in a rising interest in the automotive industry for weight reduction and engine downsizing [1,2]. The latter implies the design of smaller engines with higher specific power by raising the levels of pressure and temperature inside the combustion chambers. Cylinder heads cast using aluminum alloys can be critically affected by this change in the severity of service conditions.

Precipitation hardening is understood to be the main contributor to the mechanical properties of cast aluminum alloys [3]. Alloying with copper and/or magnesium allows the precipitation of coherent/semi-coherent, fine-sized and fine-dispersed precipitates in the aluminum α solid solution during aging heat treatments. The main precipitation hardening systems in each cast aluminum alloy family are listed in Table 1. Multiple studies point out that mechanical properties peak for microstructures containing the metastable precursors of these phases [4]. These phases are more efficient in hindering the movement of dislocations in the α-phase, which raises mechanical properties such as yield strength. During service at high temperatures, coarsening takes place (driven by the reduction of the total surface energy). Precipitates lose their coherency and progressively transform to their stable versions resulting in the loss of mechanical properties. The rate at which these metastable phases transform is -in part- governed by their thermodynamic stability at service temperatures.

One can find a myriad of attempts to optimize cast aluminum alloys in literature. Most of these studies revolve around the effect of chemical elements on the microstructure and properties of these alloys. Three categories of desired effects can be identified: (a) modification of the eutectic silicon [5–8], (b) modification of the morphology of deleterious Fe-containing intermetallics [9] and (c) precipitation of new phases with precipitation hardening potential [10–16]. Special interest has been granted to transition metals, justified by their low solubility and slow diffusion in aluminum.

However, the influence of different elements on the stability of metastable phases is not clearly identified. Indeed, the observation of these, generally very fine and well-dispersed, phases is difficult and time consuming. Complex and detailed experimental studies have to be performed in wide concentration and temperature ranges. Nevertheless, a stability increase of metastable phases with temperature should open an alternative way for the design of cast aluminum alloys having longer service life.

Therefore, the aim of this study is to show how the use of thermodynamic calculations can assist the development of novel in-service-aging resistant alloys. The direct effect of alloying elements on the thermodynamic stability of metastable hardening phases was explored. The multi-constituent character of the industrial alloys required the use of Thermo-Calc software and its TCAL4.0

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Table 1
Precipitation hardening systems in different cast aluminum alloys.

Alloy	Alloying elements (wt.%)	Precipitation hardening systems
319 (Al-Si-Cu)	>3% Cu	θ-Al_2Cu
A356 (Al-Si-Mg)	0.25%–0.5% Mg	β-Mg_2Si
A356+Cu (Al-Si-Cu-Mg)	0.5%–1% Cu 0.3%–0.5% Mg	θ-Al_2Cu β-Mg_2Si Q phase ($Al_5Cu_2Mg_8Si_6$)

Table 2
Chemical composition (wt.%) of the A356+Cu alloy used as a reference material.

Si	Cu	Mg	Ti	Ni	Sr	Fe	Other
7	0.5	0.3	<0.15	<0.05	0.01	<0.15	<0.1

aluminum database [17]. This software is based on the CALPHAD approach that calculates phase equilibria in multi-element systems using Gibbs energy minimization algorithms and relying on substantial experimental thermodynamic databases.

2. Reference material

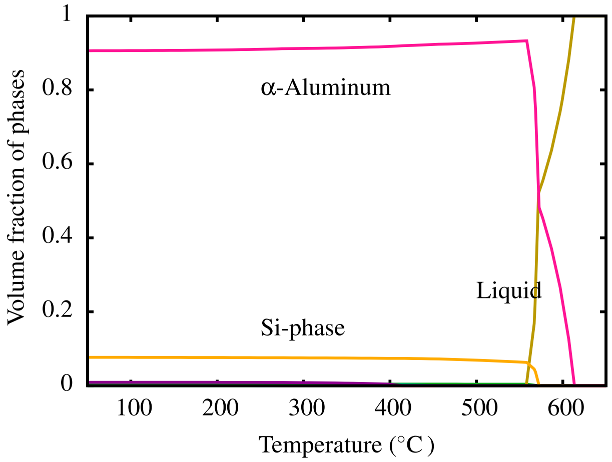
To study the influence of different alloying elements available in the TCAL4.0 database on the stability of metastable phases, a widely used A356+Cu alloy was taken as a reference material. The A356+Cu alloy belongs to the family of Al-Si-Cu-Mg alloys (Table 1) and contains usually a number of different impurities (Table 2). During solidification pro-eutectic α-phase dendrites form, rejecting excess Si into the interdendritic regions which ends up forming the Si-phase. Sr is added to promote globular over fibrous Si-phase morphology in the eutectic regions. Coarse θ-Al_2Cu and β-Mg_2Si also form during solidification. Other Fe-rich intermetallics such as β-$Al_9Fe_2Si_2$ and α-$Al_{15}Si_2(Fe,Mn)_4$ can be formed due to the presence of even trace amounts of iron in the composition. The needle-like or plate-like morphology of the β-$Al_9Fe_2Si_2$ is more deleterious to the mechanical properties than the less acicular "chinese script" α-$Al_{15}Si_2(Fe,Mn)_4$.

These alloys classically undergo a T7 heat treatment (solutionizing at ~500 °C for ~5 h, water quench, aging at ~220 °C for ~3 h). The coarse θ-Al_2Cu and β-Mg_2Si dissolve during solutionizing and precipitate during aging following the well-documented precipitation sequence (Guinier-Preston (GP) zones $\rightarrow P'' \rightarrow P' \rightarrow P$) [18]. Three precipitation sequences are expected in these alloys, resulting in the precipitation of θ-Al_2Cu and β-Mg_2Si and Q. The order of occurence of these sequences and their interactions are still a matter of discussion in the scientific community.

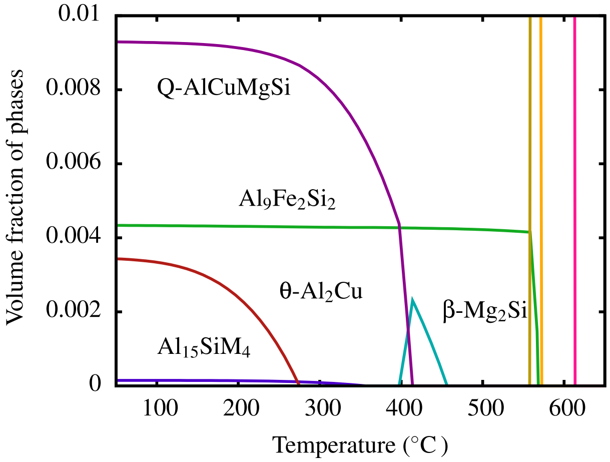
Equilibrium calculation using the composition of A356+Cu alloy and TCAL4.0 database yields the results shown in Fig. 1. All the phases reported in literature are predicted. Solvus temperatures of most of these phases were found to be in accordance with experimental results from [19–23] (Table 3).

The database validation based on the stable equilibrium state cannot be automatically extended to the metastable states, but it serves as a first confirmation that the alloy is well described. Besides, accurate data on the stability of metastable phases are rare. Furthermore, the presented results based on the thermodynamic stability of metastable phases can be extended to the stable phases, i.e. any effect (stabilizing, destabilizing) observed for θ' or β' (θ'' or β'') phases is observed for θ or β phases as well.

Therefore, the authors believe that the TCAL4.0 database can be considered as reliable to carry out thermodynamic calculations for the A356+Cu alloy including metastable states.



(a) Major phases.



(b) Minor phases.

Fig. 1. Phase volume fractions as a function of temperature at equilibrium for A356+Cu reference alloy calculated using Thermo-Calc software and TCAL4.0 database.

Table 3
Comparison between calculated and experimental values of solvus temperatures of different phases in the A356+Cu reference alloy [19–23].

Phases	Calculated	Literature data [19–23]
β-$Al_9Fe_2Si_2$	567	567.2
Si	572	577.9
Q-phase	421	421.5
β-Mg_2Si	468	441.3

Formation of the θ-Al_2Cu phase in an A356+Cu alloy is unlikely due to the low Cu content and the prevalence of the Q phase. Although this is an accepted statement, results from literature still do not confirm the complete absence of the θ-Al_2Cu phase since the precipitation sequence for the Q phase in these alloys is yet to be fully understood. Moreover, the analysis of equilibrium in A356+Cu alloy at different temperatures reported in Fig. 1 showed the presence of θ-Al_2Cu together with Q. The objective of the present work is to investigate metastable equilibria with prime and double-prime phases. The Q' phase was not considered because, to the best of the authors' knowledge, of the absence of its description in the TCAL4.0 database. Therefore, the analysis was limited to θ and β phases and their precursors.

3. Thermodynamic calculations

Thermodynamic calculations were carried out using Thermo-Calc software and the TCAL4.0 database for aluminum alloys. This

Table 4
Phases that have to be neglected to be able to analyze an equilibrium involving different metastable phases (according to the notation used in the TCAL4.0 database).

Stable phase	Metastable phase to analyze	Phases to reject
θ-Al_2Cu	θ'-Al_2Cu	AL2CU_C16, AL2CU_OMEGA, ALCU_ETA, AL3NI2, ALCU_ZETA, ALCU_EPS
	θ''-Al_3Cu	All above + THETA_PRIME, ALCU_DEL, AL10CU10FE, GAMMA_D83, FCC_L12, BCC_B2, V_PHASE
	GP zones	All above + THETA_DPRIME, AL7CU4NI
β-Mg_2Si	β'-Mg_2Si	Q_ALCUMGSI, MG2SI, AL18FE2MG7SI10, S_PHASE
	β''-Mg_2Si	All above + BETA_PRIME, B_PRIME, T_PHASE, U2_AL4MG4SI4, C14_LAVES, ETA_PRIME, Q_PHASE, C36_LAVES, T_PRIME, MG2ZN3

Table 5
Chemical elements available in the TCAL4.0 database.

Ag	Al	B	Be	Bi	C	Ca
Cd	Ce	Co	Cr	Cu	Fe	Ga
Ge	H	Hf	In	K	La	Li
Mg	Mn	Na	Ni	Pb	Sc	Si
Sn	Sr	Ti	V	Zn	Zr	

database was used since it is the first of its kind to include the thermodynamic description of metastable phases such as θ'-Al_2Cu and β'-Mg_2Si (and their double-prime versions). As stated before, these phases are of particular interest for this study. The copper-rich GP zones are also described as a different composition set of the α aluminum-based solid solution. It enables the exploration of the effect of alloying elements on these phases that are directly responsible for the mechanical properties of cast aluminum alloys.

The first step of the calculation is the retrieval of thermodynamic data from the database. The retrieved data concerns phases that are described in the database for the given system composition. Equilibrium calculations will then render the most stable phase for a given set of conditions.

The aforementioned precipitation sequence is explained by a difference in nucleation barriers between the stable phases and their metastable precursors [18]. While the stable incoherent phases have lower Gibbs energies than their coherent/semi-coherent precursors, they have higher nucleation barriers due to higher matrix/precipitate interface energy. This means that in order to calculate thermodynamic equilibria involving metastable phases, stable phases should not be taken into account for the Gibbs energy minimization. Table 4 gives the sets of phases (according to the notation used in the TCAL4.0 database) to be rejected to obtain an equilibrium involving metastable θ'-Al_2Cu, θ''-Al_3Cu and associated GP zones instead of stable θ-Al_2Cu as well as β'-Mg_2Si and β''-Mg_2Si instead of stable β-Mg_2Si.

Once the desired metastable equilibrium is established, the composition of the reference alloy was modified and the effect of alloying elements on the stability of the metastable hardening phases was investigated.

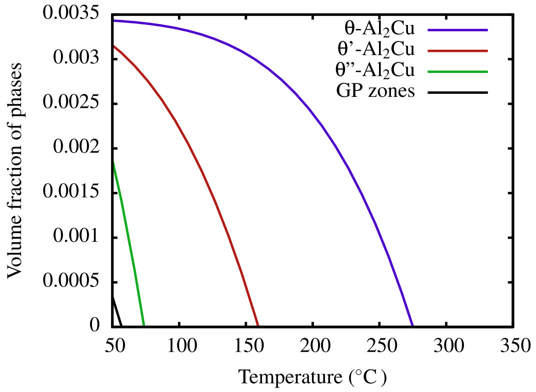
Table 5 references all the chemical elements present in the TCAL4.0 database. Some of these elements are of known deleterious effects on mechanical properties of aluminum alloys, such as H, Ga, S, P and Fe. Other elements such as Cd, Pb, Be and Bi are prohibited from use in industrial applications and were not examined in this study.

The initial system that was used is Al-Si-Cu-Mg-Mn-Fe, in which the compositions were set according to the values given in Table 2 (A356+Cu alloy).

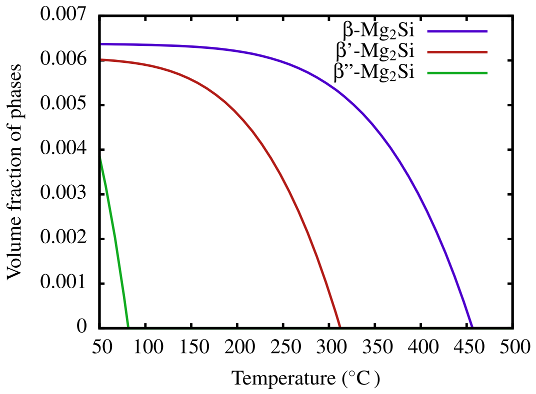
4. Results

Following the procedure described in the previous section, different levels of metastable equilibria can be calculated first for the reference A356+Cu alloy as a function of temperature for θ'-Al_2Cu and β'-Mg_2Si phases (Fig. 2). One can see that the classic precipitation sequence is successfully depicted by Thermo-Calc. GP zones as a precursor for the β-Mg_2Si phase is not well known and is therefore not present in the database. The objective here is to displace the curves of the metastable phases toward higher temperatures by adding new alloying elements. This will procure more aging resistance to aluminum alloys, since metastable phases ensuring mechanical properties would be stable at higher temperatures.

To identify stabilizing elements, the influence of a 1 wt% addition of each alloying element available in the TCAL4.0 database (except of H, Ga, S, P, Cd, Pb and Be as explained earlier) is investigated in comparison to the reference alloy. It must be understood that the choice of 1 wt% is semi-arbitrary. It is chosen as an alloying element addition that will not significantly alter the raw material cost in the manufacturing and that will also not considerably affect the general phase equilibria in the alloy. However the exact number of 1% is arbitrary and is just uniformly applied to all the tested chemical elements in order to make the comparison.

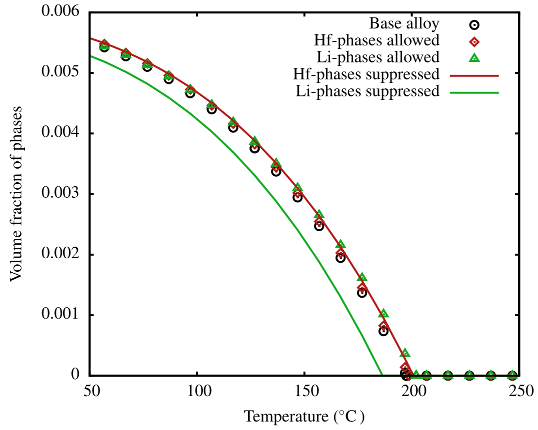


(a) θ-Al_2Cu precipitation sequence.

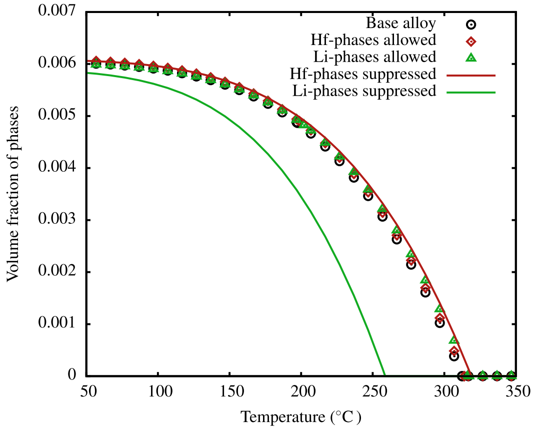


(b) β-Mg_2Si precipitation sequence.

Fig. 2. Volume fraction of stable and metastable phases as a function of temperature for the reference A356+Cu alloy.



(a) θ'-Al_2Cu.



(b) β'-Mg_2Si.

Fig. 3. Effect of an addition of 1 wt% Li and Hf in A356+Cu reference alloy on the temperature stability of metastable phases.

The results are presented in the form of the volume fraction of the metastable phases (θ'-Al_2Cu and β'-Mg_2Si) as a function of temperature. For ease of reading, the following diagrams will contain only these phases of interest.

4.1. Destabilizing and non-stabilizing elements

Fig. 3 shows the effect of Li and Hf additions in the reference A356+Cu alloy on the temperature stability of θ'-Al_2Cu and β'-Mg_2Si. Both elements are able to form new phases due to their low solubility limit in aluminum (about 1 wt% at 600 °C for Li and near zero for Hf). The advantage of thermodynamic calculations using Thermo-Calc software is that the hypothetical case when the precipitation of the new phases is hindered can be easily analyzed carrying out restrained calculations. It is possible, using certain protocols that act on the kinetics of precipitation during solidification, to avoid the precipitation of undesired phases. Therefore, two cases will be discussed henceforth (i) when the newly added element is allowed to form a new phase and (ii) when it is constrained to remain in α solid solution.

It can be seen that when constrained to remain in solution, Li has a destabilizing effect on both θ'-Al_2Cu and β'-Mg_2Si phases, decreasing their solvus temperatures by 20 °C and 50 °C, respectively, in comparison with the reference alloy. In the other case, Li seems to have little to no effect on the stability of these phases. The same behavior was observed for the double-prime versions of these phases. Studies on A380 modified by 0.1 wt% Li and A356 modified with 0.3 wt% Li reported no precipitation of Li-containing phases [5,6] thus favoring the first scenario.

Regarding Hf a different effect happens compared to what is observed for Li. In both cases, Hf seems to stabilize none of the two phases. It is also noticeable that there is very little difference between the two calculations. Hf, when added to aluminum, is known to precipitate in the form of Al_3Hf precipitates. Hallem et al. [13] reported that this phase has a metastable version with a $L1_2$ crystal structure coherent with the aluminum matrix. They suggested that such precipitates carry interesting precipitation hardening potential. It is however noteworthy that they studied alloys that contain little to no Si [16,24]. The first equilibrium calculation yields an equilibrium involving Si_2Hf. This phase and a set of other similar phases with different stoichiometry have to be rejected in order to obtain an equilibrium involving Al_3Hf. This result confirms the observations made in the aforementioned study.

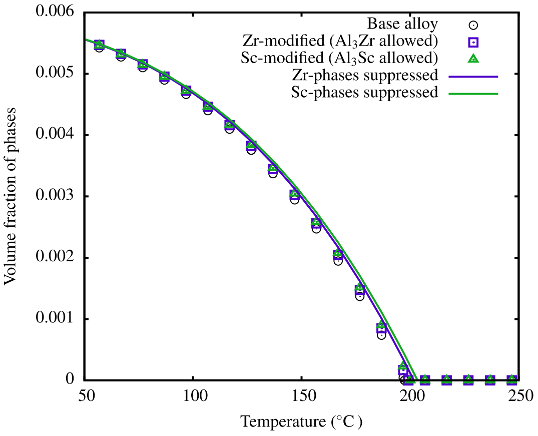
Very similar results were observed for elements such as Co and Ce. Some of these elements present a possible precipitation hardening effect. However, most of them have either no notable effect or are deleterious to the stability of the main hardening phases in the studied alloy.

4.2. Stabilizing elements

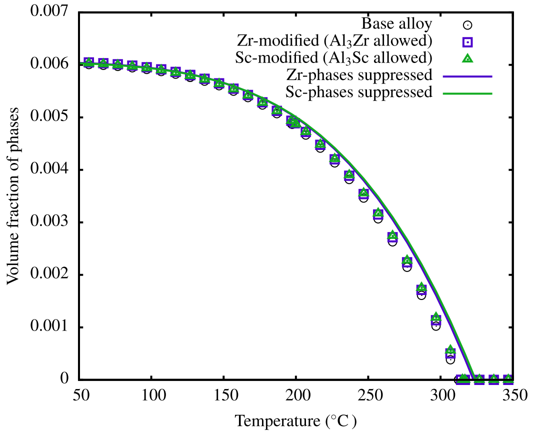
This section presents the chemical elements that have the most prominent stabilizing effect. All these elements happened to be transition metals that have low solubility and are slow diffusers in aluminum. Most of these elements precipitate in the form of peritectic Al_3X phases in aluminum binary alloys.

The effect of Zr and Sc additions in Al-Cu alloys was studied by Samuel et al. [14]. This study pointed out a significant improvement in the alloy strength and it was observed that softening due to aging was delayed by the presence of these elements. Calculations presented in Fig. 4 show that the addition of either elements stabilizes the two hardening phases in the reference A356+Cu alloy. However, the observed effect is visibly not prominent. It was also reported that Zr precipitates as Al_3Zr in two distinct crystallographic structures: stable $D0_{23}$ and metastable, coherent $L1_2$. Sc was also seen to precipitate as Al_3Sc and more complex phases when added with Zr simultaneously. Nevertheless, the increase in strength was not associated to precipitation hardening brought in by these phases, since they precipitated only during solidification. A recent study by Muhammad [25] et al. reported that grain refinement and precipitation of Al_3Sc are responsible for the increase of mechanical properties in A357 alloys modified by up to 0.4 wt% Sc.

Ti is used in cast aluminum alloys as a refiner (Ti_2B particles). Most studies focus on it as an impurity and its effect is studied in combination with other elements bearing the same status such as V and Zr. Elhadari et al. [26] modified Al-7 wt% Si-1 wt% Cu-0.5 wt% Mg alloy with 0.11 wt% Ti, 0.20 wt% Zr and 0.25 wt% V. They studied both the isolated and combined effects of these elements. It was reported that complex Si-Zr-V-Ti phases prevail over the expected binary Al_3X phases. Hernandez et al. [27] reported $(Al,Si)_2(Ti,Zr)$ and $(Al,Si)_3(Ti,Zr)$ phases in a 354 alloy modified with 0.21 wt% Ti and 0.39 wt% Zr. On the other hand, V precipitates in different binary phases such as $Al_{11}V$ [28] $Al_{21}V_2$ [6] and Si_2V [29]. Casari et al. [30] associated a slight increase in mechanical properties of a V-modified A356 alloy to an acceleration of precipitation kinetics of β-Mg_2Si. Calculations presented in Fig. 5 show the prominent stabilizing effect of Ti and V on the θ'-Al_2Cu and β'-Mg_2Si hardening phases. It is also observable that the stabilizing effect is always more pronounced in case the added elements are prohibited from precipitating in new phases.



(a) θ'-Al_2Cu.



(b) β'-Mg_2Si.

Fig. 4. Effect of an addition of 1 wt% Zr and Sc in A356+Cu reference alloy on the temperature stability of metastable phases.

4.3. Elements with unclear effects

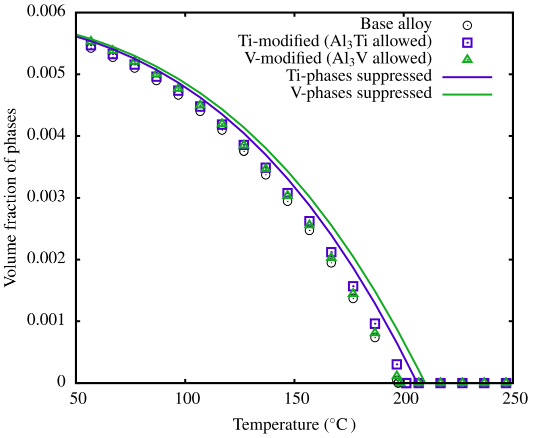
Ce, Ag, La and Zn all have possible destabilizing effects on the hardening phases. Constrained calculations could not be carried out for Ag, Ce and La, as these calculations yield irregularities such as stability of the liquid phase at room temperature.

Equilibrium calculation with addition of Ni produces the Al_7Cu_4Ni phase that replaces θ'-Al_2Cu. Al_7Cu_4Ni phase is stable up to 420 °C. This equilibrium also involves the Al_3Ni phase. Rejecting all Ni-containing phases causes the liquid phase to reappear at low temperatures. This indicates a lack of data in the TCAL4.0 database to describe such a metastable state. A destabilizing effect is observed on θ'-Al_2Cu, which is contrary to the stabilizing effect on β'-Mg_2Si.

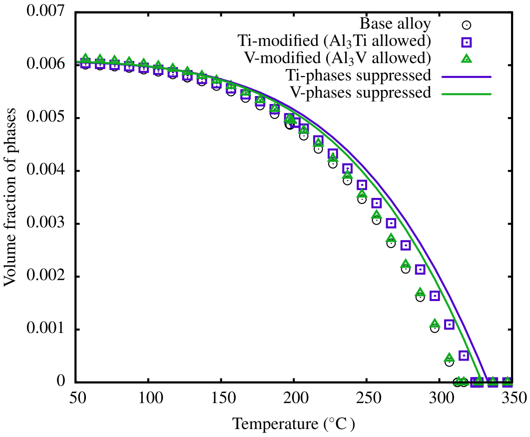
Calculations presenting such irregularities are indicated by an asterisk in the summary given in Table 6.

4.4. Summary

A full summary of the calculation results for the all studied elements destabilizing and stabilizing is presented in Table 6. The results are expressed with the difference in solvus temperatures of the θ'-Al_2Cu and β'-Mg_2Si hardening phases due to the composition modification of the reference A356+Cu alloy with 1 wt% of alloying element: $\Delta T^s_\varphi = T^{s,mod}_\varphi - T^{s,ref}_\varphi$ (where $T^{s,mod}_\varphi$ is the solvus temperature of the hardening phase in the modified alloy and $T^{s,ref}_\varphi$ is the solvus temperature of the hardening phase in the reference alloy). Negative values correspond to destabilizing effects.



(a) θ'-Al_2Cu.



(b) β'-Mg_2Si.

Fig. 5. Effect of an addition of 1 wt% Ti and V in A356+Cu reference alloy on the temperature stability of metastable phases.

One can see that the calculations when a new Al_3X phase was allowed to form suggest that Ti is the strongest stabilizer of the metastable θ'-Al_2Cu and β'-Mg_2Si phase: increase in solvus temperatures by 3 and 12 °C, respectively. For the calculations when the alloying elements were constrained to remain in solution, Ti, V, Sc, Zr and Cr have the strongest stabilizing effect.

Data about the double prime phases (θ''-Al_3Cu and β''-Mg_2Si) is presented in Table 7. Aside from some small differences, similar conclusions about stabilizing effects can be drawn.

4.5. Solvus temperatures of potentially formed Al_3X phases

According to the thermodynamic calculations, the highest metastable phases stabilization can be achieved when the formation of new Al_3X phases is hindered. Therefore, the solidification kinetics must be far from equilibrium. This must be addressed by examining the nature and solvus temperatures of the expected Al_3X phases.

Solvus temperatures being higher than the liquidus temperature means that these phases solidify directly from liquid, prior to aluminum dendrites. This can obstruct mold filters and such phases take acicular shapes that act as stress concentrators. A solvus temperature lower than the solidus temperature would make it possible for these phases to dissolve during solutionizing heat treatment while avoiding incipient melting. A subsequent aging heat treatment may potentially provide precipitation hardening.

Table 8 shows the solvus temperatures of Al_3X phases formed with the stabilizing alloying elements. Al_3Zr, Al_3V and Al_3Ti

Table 6
Summary of the thermodynamic analysis for different alloying elements available in the TCAL4.0 database as stabilizers of metastable θ'-Al_2Cu and β'-Mg_2Si hardening phases. Two types of calculations were carried out: with the formation of new phases and without formation of any new phases.

Element (X)	Element allowed to precipitate $\Delta T^s_{\theta'}$ [a] (°C)	 $\Delta T^s_{\beta'}$ (°C)	Element only in solid solution $\Delta T^s_{\theta'}$ (°C)	 $\Delta T^s_{\beta'}$ (°C)
Ti	3.2	12.5	8.8	21.2
Ni	Inexistant	1.9	−7.1*	9.6*
V	2.8	4.5	12.3	17.0
Zr	1.7	1.8	4.2	10.4
Hf	1.3	1.5	3.3	6.3
Sc	2.5	2.7	5.9	11.8
Ge	0.6	−1.3	0.6[b]	−1.3[b]
Zn	−0.9	−1.1	−0.9*	1.1*
Co	2.8	2.9	5.8	3.8
Cr	2.7	2.6	12.6	9.9
Ag	0.9	−61.5	–*	–*
Ce	1.6	1.6	–*	–*
La	0.9	1.0	–*	–*
Li	4.6	4.7	−11.0	−53.6

[a] $\Delta T^s_{\varphi} = T^{s,mod}_{\varphi} - T^{s,ref}_{\varphi}$ (where $T^{s,mod}_{\varphi}$ is the solvus temperature of the hardening phase in the modified alloy and $T^{s,ref}_{\varphi}$ is the solvus temperature of the hardening phase in the reference alloy).

[b] The two results are identical since Ge has a high solubility in aluminum, no phases involving Ge precipitate.

Table 7
Summary of the thermodynamic analysis for different alloying elements available in the TCAL4.0 database as stabilizers of metastable θ''-Al_3Cu and β''-Mg_2Si hardening phases. Two types of calculations were carried out: with the formation of new phases and without formation of any new phases.

Element (X)	Element allowed to precipitate $\Delta T^s_{\theta''}$ (°C)	 $\Delta T^s_{\beta''}$ (°C)	Element only in solid solution $\Delta T^s_{\theta''}$ (°C)	 $\Delta T^s_{\beta''}$ (°C)
Ti	0.6	0.6	7.7	22.5
Ni	Inexistant	0.8	1.1	1.0
V	0.6	0.6	10.6	17.4
Zr	0.6	0.6	3.6	10.7
Hf	0.9	0.9	2.7	6.5
Sc	1.8	1.7	4.8	11.9
Ge	1.1	1.0	1.1	1.0
Zn	1.1	1.0	1.1	1.0
Co	1.1	1.0	1.1	1.0
Cr	1.1	1.0	1.1	1.0
Ag	1.1	1.0	–*	–*
Ce	1.2	1.1	–*	–*
La	1.1	1.0	–*	–*
Li	3.2	2.9	−10.9	−40.8

Table 8
Solvus temperatures of the newly formed phases compared to the respective solidus and liquidus temperatures.

Phases	Solvus temperature (°C)	Solidus temperature (°C)	Liquidus temperature (°C)
Al_3Ti ($D0_{23}$)	432	557	622
Al_3Ti ($D0_{22}$)	721	557	721
Al_3Sc	563	552	614
Al_3V ($D0_{22}$)	670	556	670
Al_3Zr ($D0_{23}$)	783	557	783
Al_3Ni ($D0_{11}$)	569	553	610

($D0_{22}$) have solvus temperatures equal to the liquidus temperature of the alloy. It ensues that these phases will be the first to form directly from the liquid. Al_3Sc and Al_3Ni have solvus temperatures between the solidus and liquidus temperatures of the alloy. Such temperatures are too high for solutionizing heat treatments that range from 480 to 520 °C.

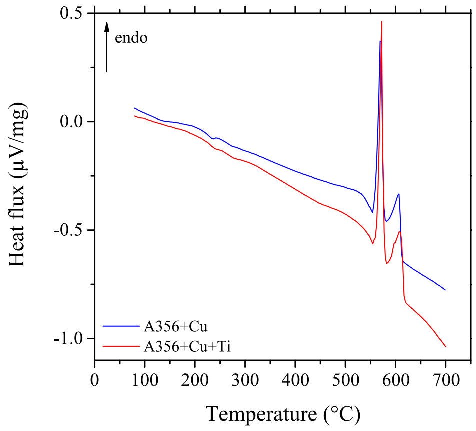
Al_3Ti in the $D0_{23}$ crystallographic structure satisfies both criteria with a solvus temperature of 432 °C. The $D0_{22}$ version of Al_3Ti is however more thermodynamically stable than $D0_{23}$. Considerations of precipitation kinetics are required to state which is more likely to precipitate.

5. Discussion

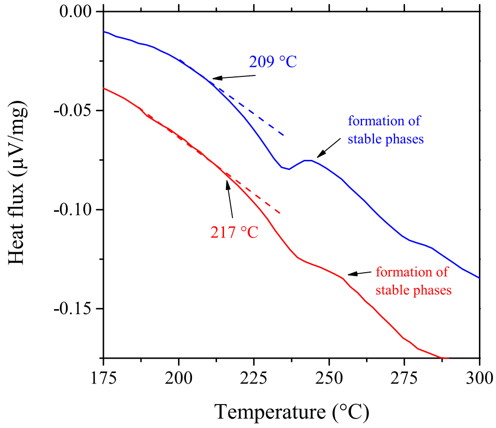
The summary of the thermodynamic calculations given in Table 6 suggests that Ti is the most efficient stabilizer of the metastable phases. Moreover, the solvus temperature of Al_3Ti ($D0_{23}$) phase is lower than the solidus temperature. To verify the theoretical predictions for the influence of Ti on the metastable θ'-Al_2Cu and β'-Mg_2Si phases, both the reference A356+Cu and A356+Cu modified by Ti alloys were cast.

To favor the formation of the metastable phases, the alloys in the as-cast state were solutionized at ~500 °C for 2 h and water quenched without further aging (T4 temper).

The influence of Ti additions on the temperature stability of the metastable phases was studied using Differential Scanning Calorimetry (DSC). DSC is a powerful and relatively easy technique which is widely used to study different precipitation sequences in



(a) Complete temperature range from room temperature to a complete melting.



(b) Temperature range where the dissolution of metastable and formation of stable phases take place.

Fig. 6. Experimental analysis by DSC of the influence of Ti additions in A356+Cu alloy on the temperature stability of metastable phases.

wrought aluminum alloys [31–33]. The real advantage of the DSC is the possibility to detect the presence of GP zones while other techniques like TEM would require special operating regimes.

NETZSCH STA 449 F3 Jupiter calorimeter was used. The experiments were carried out at a constant heating rate of 5 K min^{-1} in an Ar atmosphere to avoid sample oxidation. The Al_2O_3 powder was used as a reference material to obtain an appropriate baseline. The sample weight did not exceed 15 mg to ensure a homogeneous heating. The sample weight was continuously recorded to verify the absence of oxidation. The heating was carried out from ambient temperature up to a complete sample melting.

DSC curves for the A356+Cu and A356 alloy modified by Ti are shown in Fig. 6. Two endothermic peaks of high intensity at around 600 °C correspond to the melting of the alloy (Fig. 6a). Moreover, on can also observe a variation of heat flux around 250 °C. A zoom between 175 and 300 °C (Fig. 6b) displays two different thermal processes: exothermic and endothermic. The latter corresponds to the formation of stable phases while the former corresponds to the dissolution of the metastable phases, according to published data on wrought aluminum alloys [31–33].

Fig. 6b shows that, at temperatures close to 210 °C, Ti addition increases by 8 °C the exothermic process temperature (217 vs. 209 °C). This temperature is believed to be the dissolution temperature of a metastable phase. However, its exact nature is difficult to identify. Quenching favors the formation of GP zones. However, the temperature at which the dissolution begins (around 210 °C) is too high for GP zones. It most likely corresponds to a metastable double-prime or prime phase. The solvus temperature increases about 10 °C due to Ti addition in the reference A356+Cu alloy is measured by DSC and is in good agreement with the data reported in Table 6. As a consequence, the thermodynamic predictions regarding the influence of Ti on the metastable phases in A356 +Cu alloy seem to be in agreement with the experimental results.

6. Conclusion

The influence of different alloying elements on the temperature stability of metastable hardening phases θ'-Al_2Cu, β'-Mg_2Si and their double prime versions in cast aluminum alloys was analyzed using thermodynamic calculations carried out with Thermo-Calc software and TCAL4.0 database. The main results can be summarized as follows:

- Li, Hf, Co and Ce do not have a stabilizing effect on θ'-Al_2Cu and β'-Mg_2Si;
- V, Ti, Cr, Zr and Sc increase the solvus temperature of θ'-Al_2Cu and β'-Mg_2Si: 1 wt% addition of these elements to a A356+Cu alloy increase the corresponding solvus temperatures up to 20 °C;
- Theoretical predictions are in agreement with experimental results obtained for the Ti-modified A356+Cu alloy.

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