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NEUTRON DIFFRACTION ANALYSIS OF PHASE PRECIPITATION IN SOLIDIFICATION OF HYPEREUTECTIC Al-Si ALLOYS WITH THE ADDITION OF Cu AND Mg

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Abstract

A good understanding of the kinetics of evolution of solid phases during solidification of hypereutectic aluminum alloys is a key factor in controlling the as-cast microstructure and, in turn, enhancing the service properties of industrial alloys.

A study was performed to evaluate the solidification kinetics for two hypereutectic Al-19%Si alloys with the addition of 3%Cu and 3%Cu+1%Mg.

This study included thermodynamic calculations of the solidification process using the FactSage™ 6.2 software package, as well as experimental thermal analysis, and neutron diffraction. The study revealed kinetics of solid Al, solid Si, Al_2Cu, and Mg_2Si evolution, as well as an individual effect of Cu and Mg alloying additions on the solidification path of the Al-Si system.

Introduction

The use of hypereutectic Al-Si alloys for the most demanding applications in the automotive industry has now become commonplace. These alloys exhibit remarkable service properties under conditions of high temperature, tension and compression load cycles, and vibration, particularly where high wear resistance is requred. Some examples include engine blocks, pistons, etc. [1-7]. To a large extent, the service properties of these alloys are determined by the as-cast microstructure of the material and, as such, are very dependent on melt processing in casting operations [8-11].

Significant residual stress may frequently develop in the solidification of complex automotive components, and is affected by geometry of the castings, cooling rates and microstructure, and the phases that have evolved during solidification [7]. Multiple studies were performed on the solidification behavior of these alloys and the resulting microstructure of the cast material.

Most recently, thermal analysis [3-5] and neutron diffraction analysis [9-11] were used to evaluate the solidification kinetics under non-equilibrium and near-equilibrium conditions. In the latter reports W. Kasprzak, D. Sediako et al. demonstrated the applicability of neutron diffraction to solidification analysis of a binary hypereutectic Al-

19%Si alloy using step-wise cooling. The authors demonstrated the potential to quantify the volume fraction of primary Si and Al, as well as Si and Al in the eutectic phase using diffraction signals from solid phases as they evolved during solidification. These studies were extended into comparative analysis of solidification of the binary Al-19%Si alloy, and the same alloy modified with addition of 3%Cu [11]. As a result, these studies reveal major changes introduced to the solidification path by the addition of Cu.

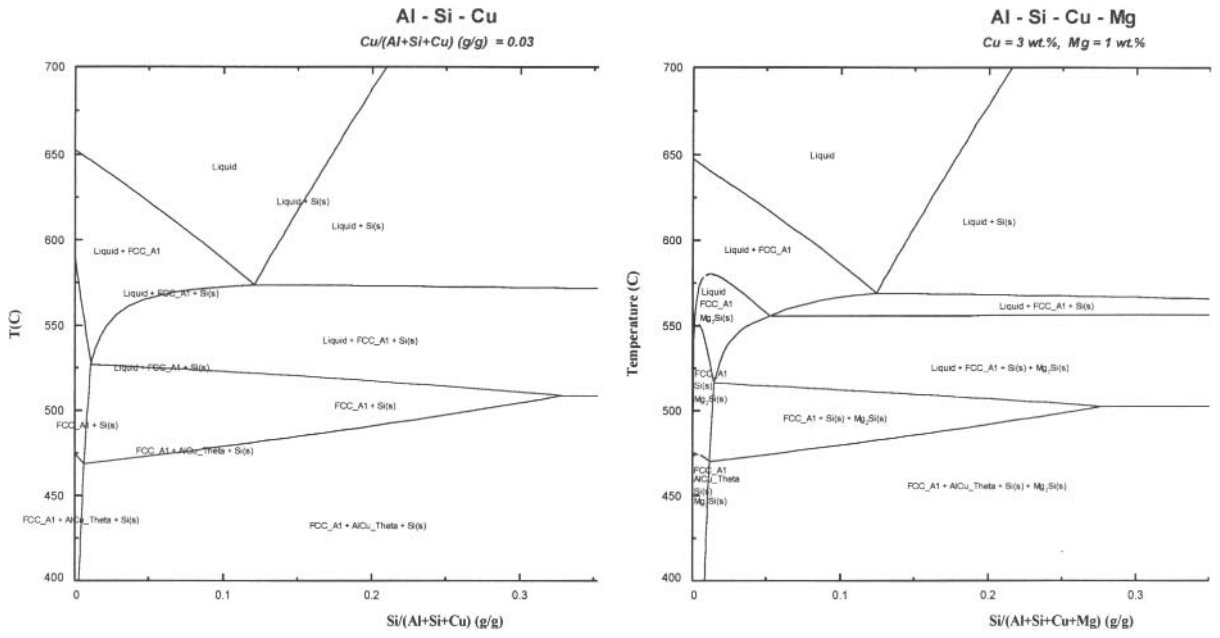
The objective of the current study is to continue this solidification analysis, extending it to a hypereutectic Al-19%Si alloy modified with the addition of 3% Cu and 1% Mg – an alloy that is similar to the one used, for example, in manufacturing motorcycle engine blocks [10]. The comparative analysis reveals changes to the solidification path caused by the addition of Mg to the Al-Si-Cu system. It is expected that such a "dissecting" approach—from Al-Si to Al-Si-3%Cu to Al-Si-3%Cu-1%Mg—will lead to a better understanding of the effect of each alloying element on microstructure formation during solidification of complex alloying systems, thus enabling alloy chemistry to be tailored, to achieve the desired as-cast microstructure.

Phase Evolution during Solidification

FactSage™ Calculations

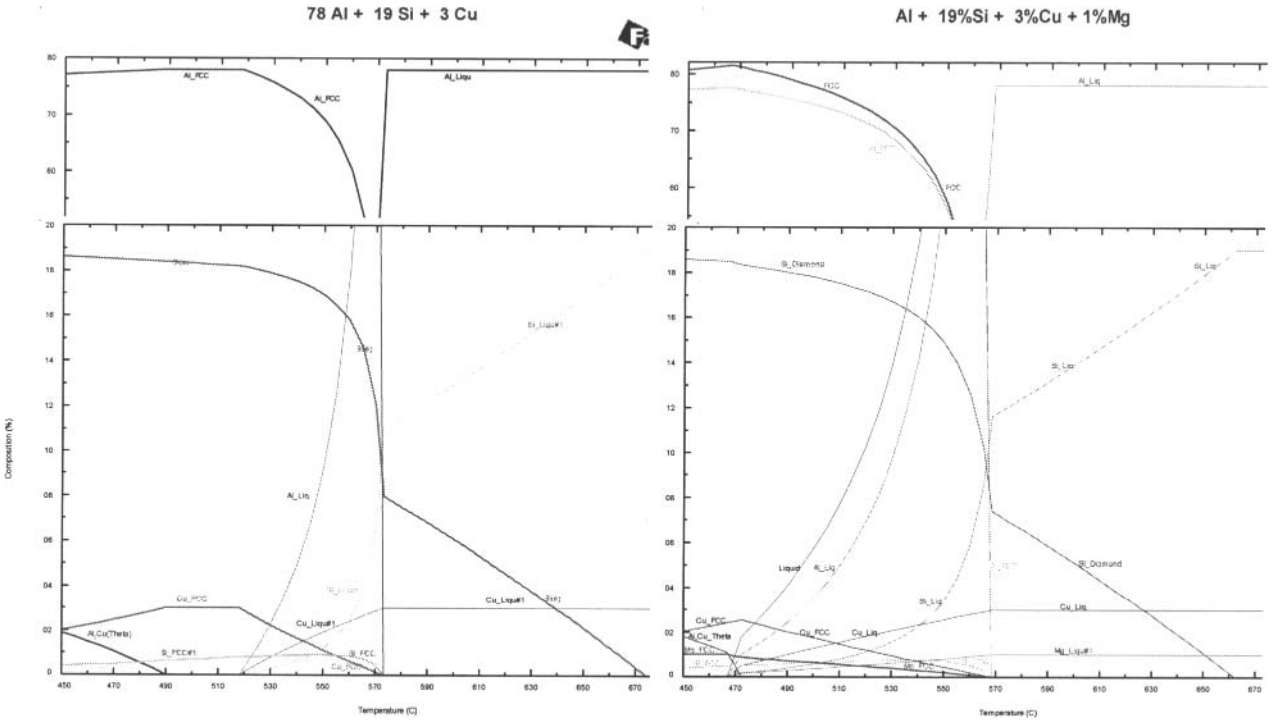
In the research presented in [11], the authors reviewed results of FactSage calculations in connection with experimental data obtained from in-situ neutron diffraction and thermal analysis experiments conducted on a hypereutectic Al-Si-3%Cu alloy. The authors demonstrated that, along with other changes, Cu addition results in the formation of up to 2% of the Al_2Cu theta phase, either soon after complete solidification (about 30°C below solidus) for equilibrium solidification, or immediately following complete solidification for the non-equilibrium process. This result was confirmed by observing notable additional energy release within the temperature range of 490-508°C in the thermal analysis [11]. The authors also showed that formation of the theta phase occurs in parallel and is coupled with reduction in Cu concentration in the FCC phase, from its maximum of 3.5% at 518°C, to 2.5% at 455°C.

Addition of 1%Mg further complicates the solidification path. As follows from the phase diagram presented in Figure1 and the equilibrium solidification presented in Figure 2, the solid FCC Mg_2Si phase starts evolving in the system about 10°C below the eutectic temperature of 568°C. When the temperature is further reduced to 475°C, Al_2Cu theta phase starts evolving concurrently with the Mg_2Si phase. The equilibrium calculations indicate that the initiation of theta phase formation occurs just prior to complete solidification of the alloy at the solidus temperature of 467°C (Figure 2, *b*). Similar to the Al-Si-Cu alloy, formation of the theta phase in the Al-Si-Cu-Mg alloy occurs at the expense of reduction the Cu concentration in the FCC phase from, in this case, a maximum of 2.9% to about 2.3% at 450°C.



(a.) *(b.)*

Figure 1. Phase diagram for Al-Si-Cu (a) and Al-Si-C-1%Mg (b.) alloys



(a.) *(b.)*

Figure 2. FactSage calculation of equilibrium solidification for ternary Al-Si-3%Cu alloy (*a.*) and Al-Si-3%Cu-1%Mg alloy (*b.*)

FactSage computation results for the non-equilibrium solidification process based on the Scheil approach are shown in Figure 3. There is an obvious disadvantage to this approach. That is, the computations end when the amount of liquid phase in the system becomes 0% and the solid-state transformations that take place below the solidus temperature may be presented as happening all at once, as shown in Figure 3. For the two alloys under analysis, theta phase evolution occurs "at once" at the solidus temperature; in both cases, the total amount of Al_2Cu is about 4%. On the contrary, the Mg_2Si phase starts forming at the end of solidification, about 10°C below the Al-Si eutectic, and its concentration just prior to the solidus temperature is 1.2%. At the solidus temperature, however, the total weight concentration of Mg_2Si is increased by an additional 0.2% to 1.4%. This increase coincides with a gradual increase in the amount of Mg and Si dissolved in the Al FCC phase to the total of 0.2% and 0.6% respectively, as shown in the zoomed-in 0-to-10% section (see Figure 3 *c.*) of the calculated path (Figure 3 *b.*).

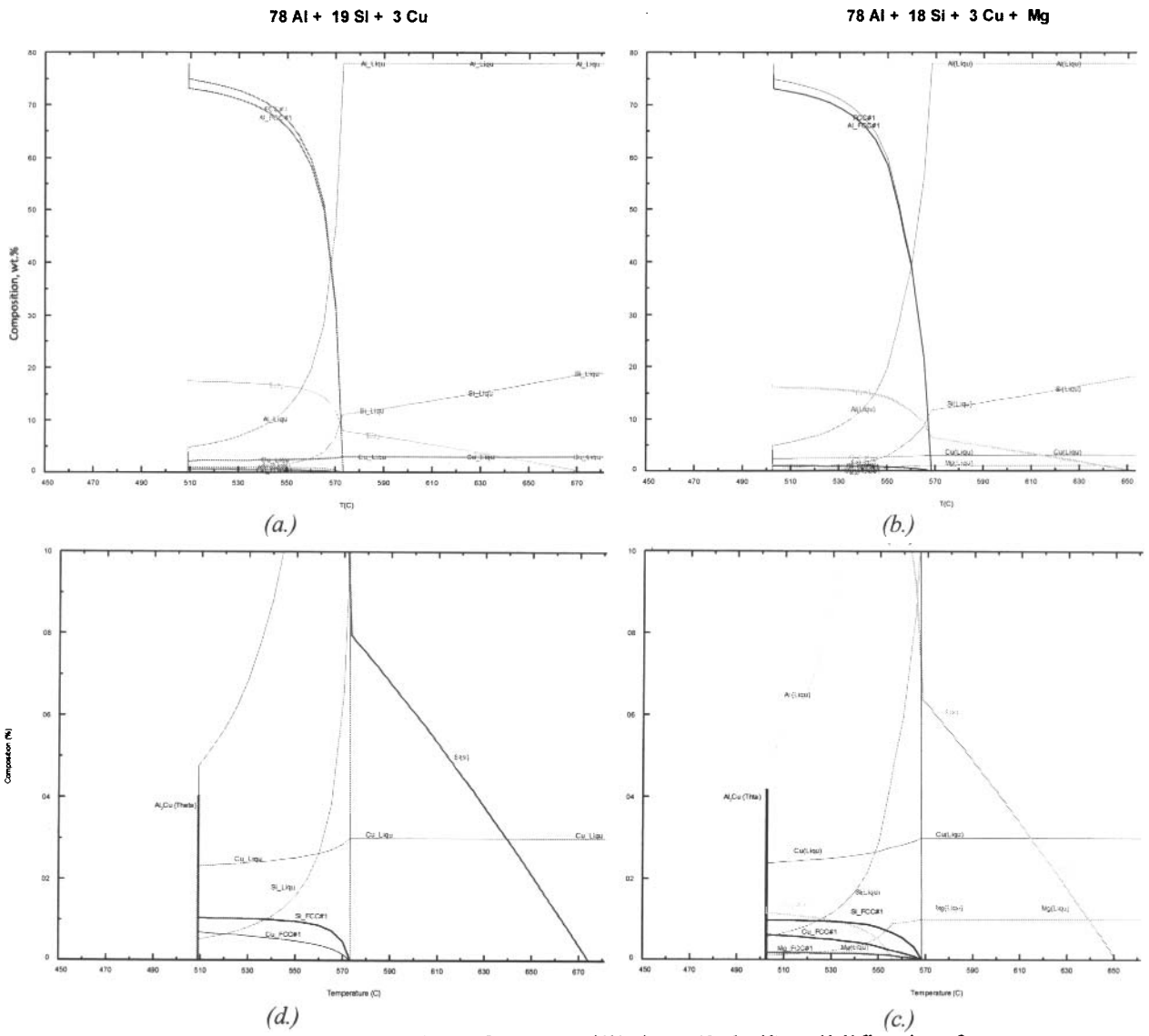


Figure 3. FactSage calculation of non-equilibrium (Scheil) solidification for ternary Al-Si-3%Cu alloy (a. and d.) and Al-Si-3%Cu-1%Mg alloy (*b.* and *c.*)

The FactSage calculation is a simulation of the complex solidification process, and is based on a number of approximations. As such, the calculations do not necessarily closely reflect the dynamics of the real solidification process of the real alloys. To gain a better understanding of the actual alloys solidification process, and also to verify the calculations, the computational analysis was performed in conjunction with thermal analysis of and in-situ neutron diffraction experiments on the solidification of the two alloys.

Thermal Analysis

The thermal analysis of the coling curves for the Al-19%Si hypereutectic alloys being studied was performed at CANMET-MTL. The analysis results are shown in Figure 4, which presents the first derivative of temperature (the cooling rate) over the temperature range of solidification. The changes introduced into the solidification path of the Al-Si system by the separate addition of, initially, 3%Cu and then 1%Mg lead to obvious differences between the curves.

First, it is clear that Cu addition caused earlier initiation of solid phase evolution (primary Si), which can be seen on both Cu-added and Cu-Mg-added alloys, compared to the binary Al-Si alloy (point 1), raising the solidus temperature by about 10°C. The addition of Cu also led to delayed formation of the Al-Si eutectic, i.e., the eutectic temperature shifted from 570°C to 562°C and 557°C, for the Cu-added and Cu-Mg-added alloys, respectively (point 2).

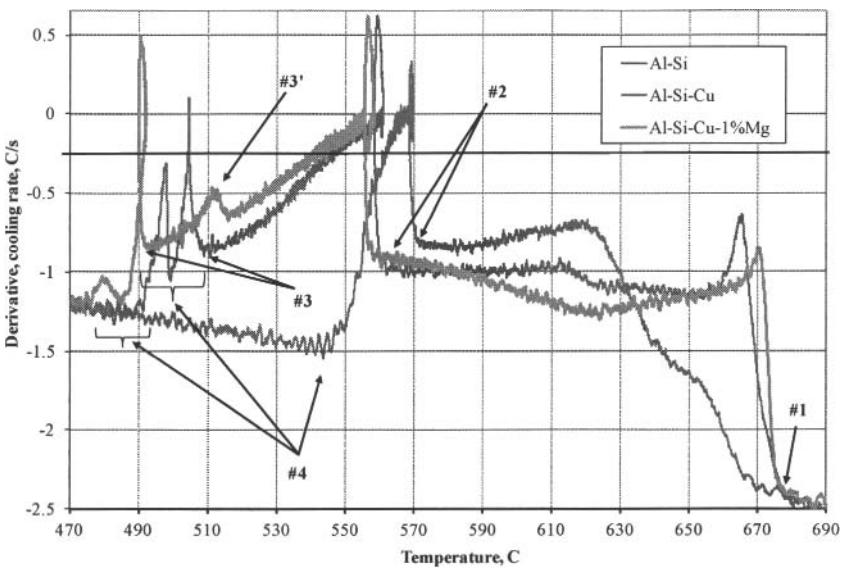


Figure 4. Cooling rate over the solidification temperatures received in the thermal analysis

The biggest effect of the alloying additions, however, can be observed towards the end of solidification, when minority phases are formed. The energy release within the temperature range of 508-495°C on the Al-Si-Cu curve (point 3) can only be attributed to

Al_2Cu theta phase formation. It is likely also true for the spike in energy release observed around 490°C on the Al-Si-Cu-Mg curve (point 3), as the theta phase is the last solid phase evolving during solidification of this alloy. This curve, however, has another area of elevated energy release, around 515 to 510°C (point 3'). According to the phase diagram, and as discuss earlier in this paper, this increase in energy release is likely due to the initiation of Mg_2Si phase formation.

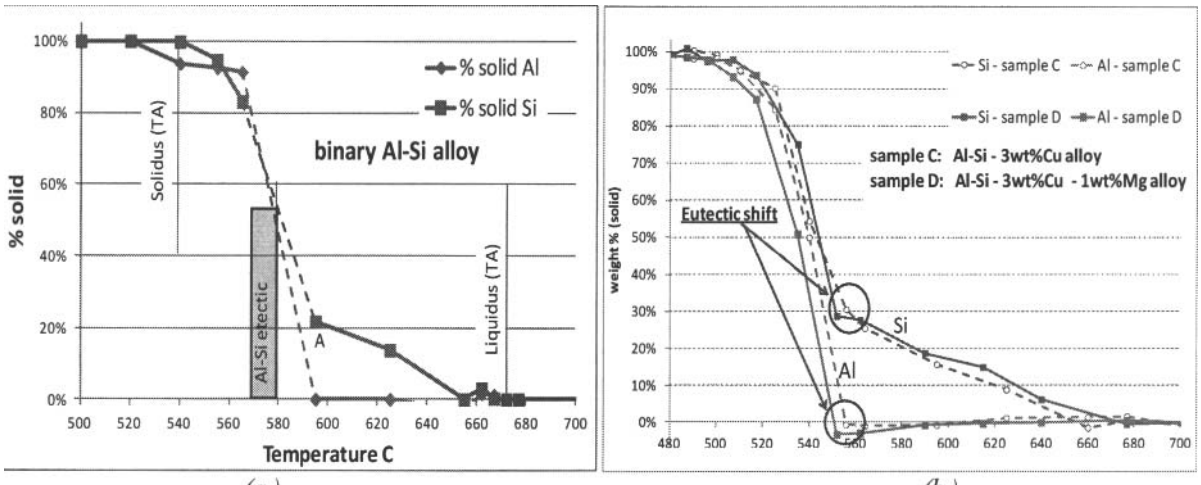
Finally, the end of solidification—solidus—can only be clearly observed for the binary Al-Si alloy (point 4) at 542°C. For the other two Cu/Cu-Mg added alloys the final stage of solidification is smeared by evolution of the minory phases, which are partially solid-state transformations. Regardless of this "smearing", it is obvious that Cu and Cu-Mg additions significantly reduce solidus temperature, by about 35°C and 45°C for the Cu-added and Cu-Mg-added alloys, respectively.

Neutron Diffraction Analysis

A detailed description of the application of neutron diffraction to the analysis of solid-phase evolution is given in our earlier papers [9-11]. The main idea of the method is the direct correlation between the normalized intensity of the diffracted monochromatic neutron beam at the specific 2TM angular range with the amount of solid phase that has a Bragg's peak within the same 2TM range.

The experiments were performed at the C2 powder diffractometer of the Canadian Neutron Beam Centre and the HB-2A neutron powder diffractometer at Oak Ridge National Laboratories. By evaluating the entire 80-degree diffraction spectrum one can retrieve the relative intensity of the Bragg peaks that correspond to the phases that evolve in the solidifying Al-Si alloy.

Figure 5 depicts the results of this type of analysis for the binary Al-19%Si alloy (Figure 5, *a.*) and Al-Si-3%Cu and Al-Si-Cu-1%Mg alloys (see Figure 5, *b.*). Based on the intensities of the Bragg's reflections, the figure shows the evolution of solid Al and solid Si over the temperature range of solidification.



(a.) (b.)

Figure 5. Solid phase evolution during solidification of the binary Al-19%Si alloy (*a.*) and Al-Si-3%Cu and Al-Si-Cu-1%Mg alloys (*b.*).

Similar to the observations made in the thermal analysis, Figure 5 shows a shift in eutectic temperature, upon addition of 3%Cu to the original binary Al-Si alloy, towards lower temperature of about 555°C (see Figure 5, *b.*, sample C).

Further addition of 1%Mg shifts the initiation of the eutectic by 7-10 degrees farther towards lower temperatures of 545~550°C (Figure 5, b., sample D). The eutectic shift can be observed on both Al and Si curves.

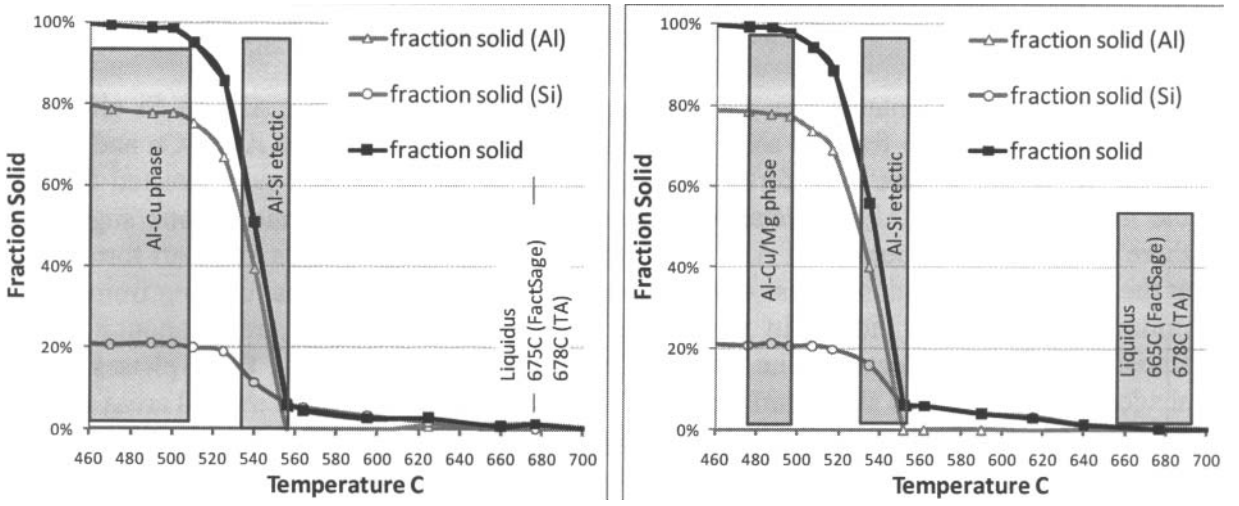


Figure 6. Fraction solid evolution for the main constituents of the alloys Al-Si-Cu (a) and Al-Si-Cu-Mg (b.)

The three-part analysis performed resulted in various temperatures of initiation of Al-Si eutectic, as well as the solidus temperature. These results are summarized in Table 1 and Table II, respectfully, below. Overall, the FactSage computations result in about an 8-13 degree higher eutectic temperature than that recorded in the thermal analysis and about an 18 degree higher temperature than that observed in the in-situ neutron diffraction.

Table I. Temperatures of initiation of Si-Al eutectic, °C

	Al-19wt%Si	Al-Si-3wt%Cu	Al-Si-Cu-1wt%Mg
FactSage™	577	573	568
Thermal Analysis	569	560	555
Neutron Diffraction	-	555	550

Table II. Solidus temperatures, °C

	Al-19wt%Si	Al-Si-3wt%Cu	Al-Si-Cu-1wt%Mg
FactSage (equilibrium)	578	518	468
FactSage (Scheil)		508	502
Thermal Analysis	542	508/490	475/495
Neutron Diffraction		~ 500	~ 480

There is also no definite answer as for the exact value of solidus temperature of the alloys (Table II). The FactSage analysis obviously results in different values for the equilibrium and non-equilibrium modes. The detection of solidus temperature in the thermal analysis is complicated by the almost simultaneous evolution of the minority phases (Al_2Cu and Mg_2Si). The step-wise approach in the in-situ neutron diffraction analysis limits the analysis to the pre-specified number of measured temperature points. Nevertheless, the results of the neutron diffraction analysis for the Cu-Mg-added alloy (480°C) came close to the lower-end solidus range determined in the thermal analysis, and also came close to the solidus value obtained in the equilibrium FactSage calculations. This value is also about 20 degrees lower than the solidus temperature observed for the Cu-added alloy.

The good statistics obtained in the neutron diffraction analysis for Al and Si allows presenting the data on fraction solid evolution during solidification of Al-Si-Cu and Al-Si-Cu-Mg alloys, Figure 6. Unfortunately, no strong diffraction signal was detected from the minority phases (Al_2Cu theta, Mg_2Si), although the FactSage calculations suggest there may be up to about 4% of Al_2Cu and up to 1.4% of Mg_2Si phases that start forming at the end of solidification. These observations may mean that the signal coming from the minority phases was hidden in the background and/or was now strong enough for statistically-viable detection. The temperature ranges for evolution of these phases are shaded in Figure 6. The slight variations in Al and Si content within the shaded areas may be related to the formation of Al_2Cu and Mg_2Si, although a much longer counting time must be used in in-situ neutron diffraction, to reliably detect the evolution path for these phases.

Conclusions

1. A "dissecting" approach to studying the solid phase evolution during solidification of hypereutectic Al-Si alloys was employed in this study. The one-at-a-time addition of alloying elements (3%Cu, followed by 1%Mg) into the high-purity binary alloy allowed for the observation of changes introduced into the solidification pattern by the separate additions. The non-equilibrium solidification of a hypereutectic Al-Si-Cu alloy was studied by computational analysis using FactSage 6.2 software, as well as by thermal analysis, and in-situ neutron diffraction analysis.
2. The three-part analysis performed resulted in the observation of various temperatures of initiation of the Al-Si eutectic. The FactSage computations, in general, result in 8~13 degrees higher eutectic temperatures than those recorded in the thermal analysis, and about18 degrees higher temperatures then those observed in the in-situ neutron diffraction analysis. This finding suggests that relatively slow cooling during thermal analysis reduced the eutectic temperature of the alloys— even slower, step-wise reduction in temperature during in-situ neutron diffraction further delays the initiation of eutectic solidification.
3. No definite answer was found for the exact value of the solidus temperature of the alloys. The FactSage analysis obviously results in different values for the equilibrium and non-equilibrium modes. The detection of solidus in the thermal analysis is complicated by the almost simultaneous evolution of the minority phases (Al_2Cu and Mg_2Si). The step-wise approach in the in-situ neutron diffraction limits the analysis to

the pre-specified number of measured temperature points. Nevertheless, the results of neutron diffraction analysis for the Cu-Mg-added alloy (480°C) came close to the lower-end solidus range determined in the thermal analysis, and also came close to the solidus value obtained in the equilibrium FactSage calculations. This value is also about 20 degrees lower than the solidus temperature observed for the "just"-Cu-added alloy (about 500°C).

4. The in-situ neutron diffraction revealed the individual profiles of solid Al and solid Si evolution. The analysis showed that the solid phase was present in the diffraction pattern as solid Si until the temperature reached 540°C for the Al-Si-Cu alloy and 535°C for the Al-Si-Cu-Mg alloy, when solid Al was first detected.
5. No strong diffraction signal was detected from the minority phases (Al_2Cu theta, Mg_2Si), although the FactSage suggests there may be up to ~4% of Al_2Cu and up to 1.4% of Mg_2Si phase that start forming at the end of solidification. These observations may mean that the signal coming from the minority phases was hidden in the background and/or was now strong enough for statistically-viable detection. The slight variations in Al and Si content within the shaded areas in Figure 6 may be related to the formation of Al_2Cu and Mg_2Si, although a much longer counting time must be used in in-situ neutron diffraction to reliably detect the evolution path for these phases.
6. The FactSage computations revealed that the Al_2Cu theta phase should form following complete solidification of the alloy. This was confirmed in thermal analysis, as a noticeable energy release was detected within the temperature range of 508~492°C. This energy release was explained by an enthalpy change associated with the formation of the Al-Cu phase.
7. The FactSage computations also revealed that the Mg_2Si phase should be forming at the end of solidification of the Al-Si-Cu-Mg alloy. The energy release observed in thermal analysis in the temperature range of around 515~510°C was associated with the initiation of Mg_2Si phase formation.

References

1. J. L. Jorstad, "The Progress of 390 Alloy: From Inception until Now", AFS Transactions, 2009, 241-249.
2. Y. P. Telang, "Process Variables in Al-21Si Alloys Refinement", AFS Transactions, vol. 71, 232-240 (1963).
3. W. Kasprzak, J. H. Sokolowski, H. Yamagata, M. Sahoo, H. Kurita, "The Effect of the Melt Temperature and the Cooling Rate on the Microstructure of the Al-20%Si Alloy used for Monolithic Engine Blocks", International Journal of Metalcasting, vol. 3, Issue 3, Summer 2009, 55-73.
4. H. Yamagata, H. Kurita, M. Aniolek, W. Kasprzak, J. H. Sokolowski, "Thermal and Metallographic Characteristics of the Al-20%Si High-Pressure Die-Casting Alloy for Monolithic Cylinder Blocks," Journal of Materials Processing Technology, vol. 199, no. 1-3, 84-90 (2008).
5. H. Yamagata, W. Kasprzak, M. Aniolek, H. Kurita, J. H. Sokolowski, "The Effect of Average Cooling Rates on the Microstructure of the Al-20%Si High Pressure Die

Casting Alloy used for Monolithic Cylinder Blocks", Journal of Materials Processing Technology, vol. 203, 333-341 (2008).

6. J. L. Jorstad, D. Apelian, "Hypereutectic Al-Si Alloys: Practical Casting Considerations", International Journal of Metalcasting, vol. 3, Issue 3, Summer 2009, 13-43.
7. D. Sediako, F. D'Elia, A. Lombardi, A. Machin, C. Ravindran, C. Hubbard, and R. Mackay, "Analysis of Residual Stress Profiles in the Cylinder Web Region of an As-Cast V6 Al Engine Block with Cast-In Fe Liners Using Neutron Diffraction", SAE International Journal of Materials and Manufacturing, June, 2011, pp. 138 - 151
8. G. I. Eskin, D. G. Eskin, "Some Control Mechanism of Spatial Solidification in Light Alloys", Zeitschrift fur Metallkunde, vol. 95, no. 8 (2004).
9. W. Kasprzak, D. Sediako, M. Sahoo, M. Walker, I. Swainson, "Characterization of Hypereutectic Al-19%Si Alloy Solidification Process using In-Situ Neutron Diffraction and Thermal Analysis Techniques", Proceedings of TMS 2010, Supplemental Proceedings: Volume 1, Materials Processing and Properties, pp. 93-104.
10. W. Kasprzak, D. Sediako, M. Walker, M. Sahoo, and I. Swainson, "Solidification Analysis of an Al-19 Pct Si Alloy Using In-Situ Neutron Diffraction", Metallurgical and Materials Transactions A, Volume 42A, July 2011, pp. 1854 - 1862
11. D. Sediako, W. Kasprzak, I. Swainson, and O. Garlea, "SOLIDIFICATION ANALYSIS OF Al-Si ALLOYS MODIFIED WITH ADDITION OF Cu USING IN-SITU NEUTRON DIFFRACTION", The Minerals, Metals & Materials Society, TMS, San Diego, CA, February, 2011, Aluminum Alloys: Fabrication, Characterization and Applications, Supplemental Proceedings: Vol.2: Materials Fabrication, Properties, Characterization, and Modeling , pp. 279-289.