

## Selecting the Optimum Mg and Si Content for 6xxx Series Extrusion Alloys

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Alloy development at the laboratory or pilot stage is often well targeted for the property requirements and generic fabrication routes of end-use applications. There may, however, be competing requirements or constraints related to production and marketing of the required primary aluminium alloy products and/or semi-finished products. Broader issues of product specification changes, intellectual property, competitiveness and marketing strategy, are best considered at a relatively early stage of alloy development. Notwithstanding all of these factors, step-change in the design of conventional alloys is still possible through emerging techniques for the understanding of precipitation. In this paper, some of the research underpinning the recent improvement of 6060/6063 alloys is discussed with reference to the shift towards lower magnesium to silicon ratios for improved strength and extrudability in Al-Mg-Si alloys.

**Keywords:** extrusion, alloy development, Al-Mg-Si, 6xxx, precipitation.

### 1. Mg and Si content in 6063 alloys

The conventional alloy code AA6063 must at first glance seem puzzling to someone new to 6xxx aluminium alloy development (Fig.1). The range of Mg and Si contents is very broad. To use the nomenclature still common in Japan, the lowest and highest alloy contents, *balanced with respect to* the atomic ratio in the equilibrium phase  $Mg_2Si$ , range from Al-0.71wt%Mg<sub>2</sub>Si to Al-1.42wt%Mg<sub>2</sub>Si.

The highest excess Mg, Al-0.55wt%Mg<sub>2</sub>Si-0.55wt%Mg, the highest excess Si, Al-0.71wt%Mg<sub>2</sub>Si-0.34wt%Si, and the nominal mid-point of the AA6063 code, namely Al-1.1wt%Mg<sub>2</sub>Si, have about the same total Mg+Si content. Nevertheless, a major part of the general purpose 6063 extrusion alloy production today has typical compositions around 0.5wt%Mg and 0.4wt%Si [1], that is, with lower alloy content than nominal and with a small *excess of Si*, namely Al-0.8wt%Mg<sub>2</sub>Si-0.1wt%Si.

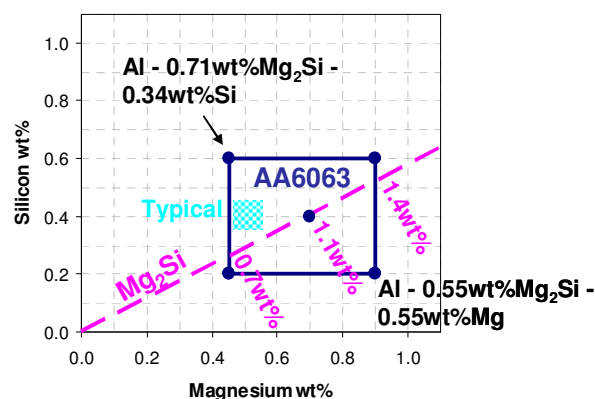


Fig. 1 Illustration of nominal Mg and Si content for the AA6063 alloy code, showing Mg<sub>2</sub>Si balanced alloys 0.7-1.4wt%Mg<sub>2</sub>Si, typical alloys and extremes of excess Mg & Si with respect to Mg<sub>2</sub>Si.

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## 2. Preference for 6063 with excess Si

The preference for these typical compositions dates back to the late 1980's to early 1990's during which time they evolved from internal R&D work by primary metal producers and/or extruders, conscious of maximizing productivity. In simplistic terms, an optimized 6063 extrusion alloy had the lowest *total Mg+Si content* consistent with the practical process requirements to exceed the minimum standard T6 properties for extrusions [2]. The lower total Mg+Si alloy content was then exploited to increase the extrusion speed limit, as a result of reduced flow stress (less adiabatic heat generated) and increased melting temperature (widening the extrusion temperature operating window). The lower alloy content might also have favored control of coarse precipitates, break-out pressure, quench sensitivity and formability.

The importance of excess Si, or rather, changing the ratio of Mg to Si in the alloy, is apparent from some of the often referenced contour plots of tensile properties for a wide range of Mg and Si contents [3, 4]. Two redrawn examples are shown in Fig.2 on which, as is customary, the line for balanced  $Mg_2Si$  is shown. With the benefit of hindsight, two features have been added here, lines of constant Mg+Si content and arrows indicating the apex (or rather trough) of the smoothed contours. Within the range of data available and at least under the conditions of sample preparation, heat treatment, etc. used to generate the property data, these arrowed points represent the lowest *total Mg+Si content* to achieve a given property level. All such points lie well into the excess Si region, and by comparison with Fig.1, largely beyond the conventional 6063 range.

The graphs are suggestive, though not convincingly, of alloy Mg to Si ratios close to one, being optimized for strength and minimum total alloy content. A comprehensive summary of the metallurgical factors effecting extrudability [5], shows that optimising the Mg to Si ratio was not, at that time, a focus of commercial alloy development.

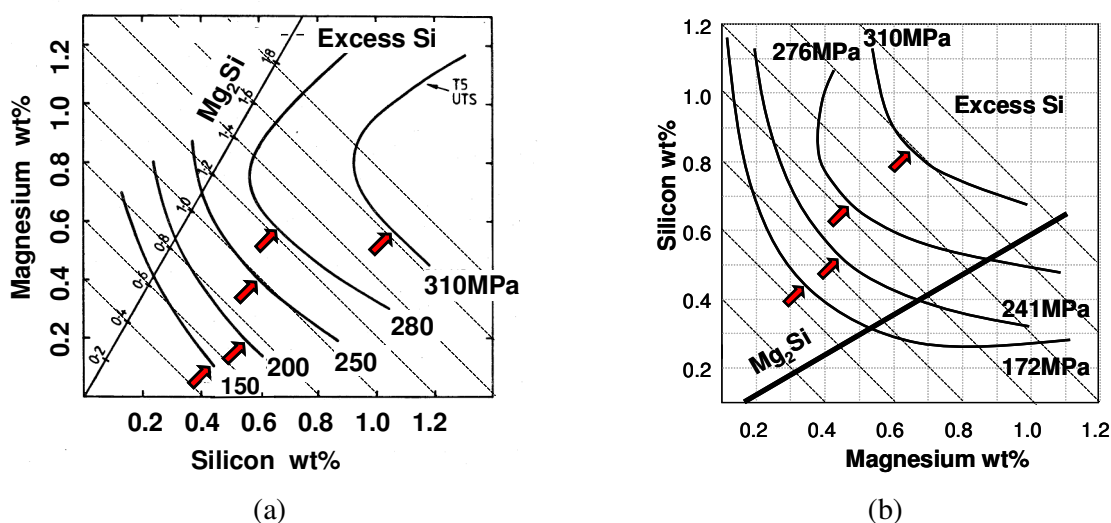


Fig. 2 (a) T5 tensile strength [3] and (b) T6 tensile strength [4] contours for Al-Mg-Si alloys, redrawn to highlight that the minimum total Mg+Si content (arrowed) to achieve a particular strength level, occurs for alloys with excess Si with respect to  $Mg_2Si$ .

Having made the point about excess Si, it is also worth noting that the contours in Fig. 2 are relatively flat, especially if excess Mg and extremes of high alloy content are excluded. A broad study, or one which excluded the alloy extremes, would therefore be likely to see a strong relationship between properties and total Mg+Si alloy content.

Two disparate examples of this are shown in Fig. 3. In the first example, the peak-aged hardness data from ageing curves [6] for five balanced alloys and four with an addition of 0.4wt% excess Si

can be seen to follow a simple parabolic relationship with a reasonable correlation ( $r^2=0.92$ ). The ternary Al-Mg-Si alloys were made by hot and cold rolling ingots prepared from pure elements and ageing curves were determined at 200°C after solution treatment at 575°C/1h.

In the second example, which is an extension of work reported in [7], the properties of twenty-three alloys, spread across 0.4-1.6wt%Mg<sub>2</sub>Si with 0-0.4wt% excess Si, were compared. The quaternary Al-Mg-Si-0.1wt%Fe alloys were prepared from commercial alloying additions, direct chill cast, extruded, solution treated at 520°C/1h, CWQ, pre-aged 24h at RT (T4), then aged to peak at 185°C (T6). The hand-fitted curves on the graph indicate the monotonic increase in hardness, for both heat-treatments, with total Mg+Si content. The flattening of the curves at high alloy content is, at least in part, a consequence of exceeding the maximum solubility of Mg and Si at the relatively low solution temperature.

Considering both examples, it is no surprise that total Mg+Si content has traditionally provided a qualitative approach to the trade-off between properties and extrusion processing for the low to medium strength 6xxx series extrusion alloys.

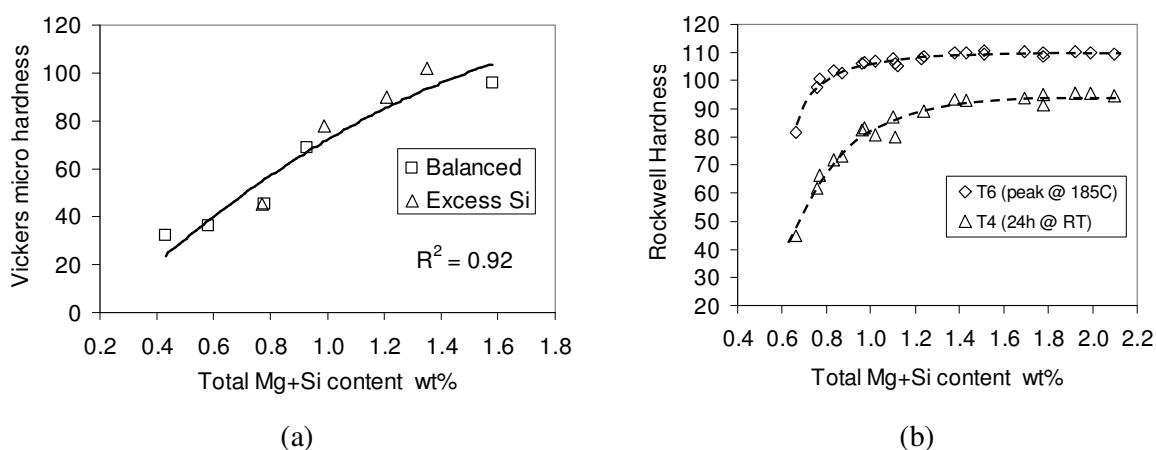


Fig. 3 Hardness of Al-Mg-Si alloys illustrating that over a wide range of Mg and Si contents the properties vary consistently with the total Mg+Si content, as shown in (a) Vickers micro-hardness of nine peak-aged alloys [6] and (b) T4 and T6 Rockwell hardness of twenty-three alloys [7].

### 3. Microstructural complexity of precipitation in Al-Mg-Si

The reasons for the benefit of excess Si over a balanced or excess Mg composition, such as indicated in Fig. 2, were not well understood. The prevailing assumption at the time, that the composition of metastable precipitates responsible for strengthening was the same as the equilibrium Mg<sub>2</sub>Si, made it difficult to explain how an addition of Si to an alloy balanced with respect to Mg<sub>2</sub>Si resulted in increased strength. The presumption was that Si caused some change to the nature of the precipitates, with explanations initially focusing on a nucleation controlled refinement of their size and distribution, though explanations were emerging [8-10] that directly linked changes in precipitate compositions to the amount of precipitation as will be expanded on below.

A wealth of knowledge and understanding has since been generated about the unexpected complexity (crystal structure, sequence, stoichiometry, etc.) of metastable strengthening precipitates in even the simplest Al-Mg-Si alloys [11-16]. Often studies compared the precipitate reactions, age hardening, microstructure and mechanical properties as a function of various heat-treatments (including thermo-mechanical) using a variety of techniques (resistivity, DSC, XRD, TEM etc.) A base alloy composition balanced with respect to Mg<sub>2</sub>Si (e.g. Al-1.0wt%Mg<sub>2</sub>Si) was often compared with alloys having excess Si or excess Mg alloys, formed by *additions to the base alloy*. Understandably, the focus has mostly been on excess Si alloys. In these types of comparison, the ratio

of Mg to Si in the alloy is varied but so too is the total Mg+Si alloy content. The optimum Mg to Si ratio for a given total Mg+Si content, based on the required properties *and extrudability*, is therefore not readily apparent.

Invariably, the more potent strengthening effect from an addition of excess Si to a base alloy, compared to the same addition (by wt%) of Mg, was confirmed. The types of metastable precipitates, their sequence of formation with ageing and their relative numbers changed dramatically from balanced to increasing excess Si (increasing total alloy content). To help describe the various precipitates it is convenient to refer to the reaction sequence that has, in the past, been considered to encompass the Al-Mg-Si alloys [17]:

SSSS (supersaturated solid solution) → Clustering → GP-I → GP-II →  $\beta''$  →  $\beta'$  →  $\beta$  ( $\text{Mg}_2\text{Si}$ ).

At the earlier stages of ageing (clustering and GP zones), a fascinating array of compositions and structures has been reported for a range of alloys, based on HRTEM, AP, etc. [14, 18, 19], and their importance as pre-cursors to later stages of ageing is becoming clearer. At the final stage of ageing, for high temperature and/or long ageing times, the excess Si alloys form Si particles in addition to  $\beta(\text{Mg}_2\text{Si})$  and a Mg rich intermediate phase has been observed in excess Mg alloys.

The critical (for alloy design) peak-aged condition is characterized by some proportion<sup>2</sup> of  $\beta''$  and  $\beta'$  phases [20]. There are distinct differences in the crystallography as well as compositional differences of  $\beta''$  when comparing balanced and excess Si alloys. There is also a dramatic difference between balanced and excess Si alloys at the  $\beta'$  stage. Adopted designations and measured precipitate compositions in ternary Al-Mg-Si alloys [13], showing only the Mg:Si atomic ratio for simplicity, are as follows (see also [21, 22] for comparison of nomenclature and stoichiometries):

- alloys balanced with respect to  $\text{Mg}_2\text{Si}$  (and similarly for excess Mg):  $\beta'$  (1.7:1)
- excess Si alloys:  $\beta'$  (1.7:1), Type B (0.4:1), Type A (0.2:1), Type C (1:1)

The relative amount of these metastable precipitate types, at the peak-aged condition, changes with excess Si [15]. Increasing excess Si (whilst also increasing total Mg+Si content) favors a shift from  $\beta'$  to the more Si-rich Type B then to Types A & C. Note, that this quantitative data is for peak-aged at 250°C (i.e.  $\beta''$  not present). Complexes of more than one type have been observed. The effect of pre-ageing on age hardening has been studied and deformation has been found to have a notable effect on the precipitate types that form and the age hardening [6, 23].

The reason for the precipitation in excess Si alloys having a more potent strengthening effect is still unclear, though in some work this has been related to the number density of precipitates. Logically, a change in precipitate composition could alter the volume fraction and/or number of precipitates formed from a given amount of Mg and Si. In this context, it should also be noted that some precipitates have been reported to contain Al in addition to Mg and Si.

#### 4. How to select an optimized Al-Mg-Si alloy

The complexity of precipitation includes crystallographic type, orientation, shape, size, number and composition all of which have been shown to change with heat-treatment and Mg and/or Si content! The question then, is how to move forward with predictive alloy selection, in light of this complexity.

One attempt to do this [7] was made by testing the hypothesis that the strengthening in peak-aged Al-Mg-Si alloys is determined by the amount of precipitation, based on a single composition of the

<sup>2</sup> At least for balanced alloys [20] it is clear that at *peak-aged* condition, the  $\beta'$  stage predominates when the ageing temperature is higher (with shorter ageing time and lower peak hardness), whilst for lower ageing temperatures (longer ageing times and higher peak hardness) the  $\beta''$  stage predominates. The proportion is also shifted to the earlier stage for higher alloy contents in balanced alloys. Similar trends are likely for excess Si alloys.

precipitates,  $Mg_xSi$ , where “x” was allowed to be varied from the assumed value of “2” from the stoichiometry of the equilibrium phase. Support for the hypothesis was gleaned from experimental studies like those in Fig.2, as well as from early reported suggestions and measurements showing that the composition of transitional and metastable precipitates in various 6xxx series alloys was more Si rich than expected. The hypothesis was shown to best represent experimental data when “x” was close to “1”.

What follows from the hypothesis is a model in which optimum alloys, based on the premise of minimum total Mg+Si content for improved extrudability, are those in which the available Mg and Si is most closely matched to the Mg and Si required to form precipitates responsible for strengthening in the peak-aged condition [24]. With the benefit of hindsight, one can see that the concept of ideal  $Mg_xSi$  precipitates is similar to an idealized *average* of various precipitate types and compositions or put another way, indicative of the most *effective* of the various precipitates types and compositions for peak-aged strengthening.

Some of the more obvious refinements to the model account for Mg and or Si that is not *available* for precipitation. An example of this is the Si *tied-up* in AlFe(Mn)Si intermetallics in commercial 6060 and 6063 alloys. Thus the ideal Mg to Si ratio for the precipitation needs to be carefully distinguished from the required Mg and Si content (and hence Mg to Si ratio) of the alloy. The model can be extended [25] to include alloys with additions of Cu (6061) and Mn (6351/6082) by determining the Mg and Si available for precipitation strengthening with an ideal ratio of Mg to Si (Fig. 4).

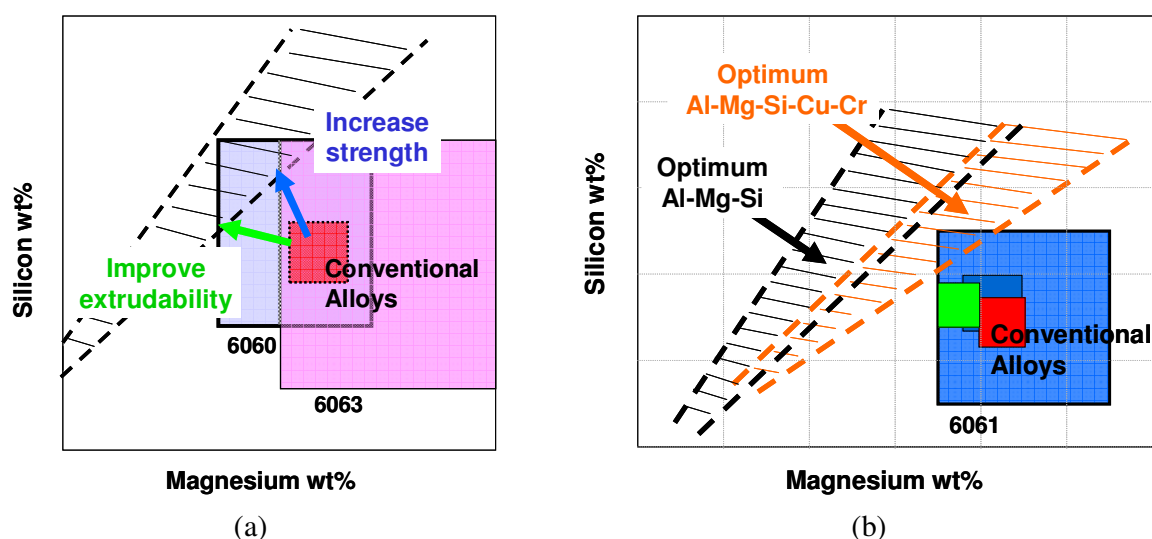


Fig. 4 Schematic showing the application of the peak-aged strengthening model for optimum extrudability in which the ideal ratio of Mg and Si available for precipitation strengthening is (a) shifted from 2:1 to 1:1 for 6060 and 6063 alloys and (b) with the model extended to include the 6061 alloy code.

From Fig. 4 it is apparent how the conventional alloy codes may have turned out to be a constraint on the selection of optimized alloys, requiring the careful introduction of new codes to exploit the developments. Alloys 6060 and the more recent 6360 [26] are good examples of the shift away from 6063 driven by the improvement with a shift to lower Mg to Si ratios. A range of extrusion alloys have been successfully commercialised based on this approach [25, 26]. Indeed the approach is not limited to the case of optimum strength versus extrudability but can be extended to select optimized alloys for any given set of performance requirements.

## 5. Summary

In broad terms, the total Mg+Si content in Al-Mg-Si alloys determines the peak-aged hardness, whilst there is significant value in minimizing the alloy content to improve extrudability. It is also clear that for a given total Mg+Si content, alloys with similar Mg and Si content (i.e. excess Si with respect to Mg<sub>2</sub>Si), provide a substantial improvement by maximizing the properties for a given total alloy content, or by minimizing the total alloy content to achieve required properties. The detailed understanding of the precipitate types, amounts and actual compositions is providing a sound basis for further refinement and new 6xxx alloy development.

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