INFLUENCE OF SOLUTE CONTENT ON GRAIN SIZE IN BINARY CU ALLOYS

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ABSTRACT

It is well accepted that grain refinement requires both, nucleation and some solute in the melt to restrict growth. The growth restriction potency of alloying elements is expressed by the growth restriction factor $Q$. As there is still a lack of detailed fundamental investigation of the effect of alloying elements on grain size in Cu alloys, the objective of this study is to provide thermodynamic-based determined $Q$-values of the alloying elements of the Cu-system. To evaluate the influence of solute content, respectively $Q$ on grain size in binary Cu alloys, initial results of melting experiments under defined cooling conditions of the TP-1 grain refiner test are shown.

INTRODUCTION

In alloy castings a fine and equiaxed grain structure is desirable [1], resulting in an improved castability and higher mechanical properties. In detail, a fine grain size leads to an improved yield strength and toughness [2], reduces the size of defects, e.g. microporosity [1] and furthermore reduces the tendency of hot tearing and cracking [3]. The grain size is dependent on the cooling rate, the solute level of alloying elements and the total number of potent nucleants [4]. A fine and equiaxed grain structure can be achieved either by fast cooling, resulting in a higher degree of undercooling [2], by increasing the number of potent nucleants or by agitation of the melt, noteworthy electromagnetic stirring and ultrasonic treatment [5].

However, among all these methods, grain refinement by inoculation by the addition of inoculating particles [1-4] has become the most common one. However, nucleation on particles added to the melt by master alloys can occur only if the melt is sufficiently undercooled [6]. For effective grain refinement there has to be some solute in the melt to restrict growth. The growth restriction parameter ($Q$) is the parameter that describes the influence of the alloying elements on the grain size that promote undercooling and nucleation by providing a larger constitutional undercooling for more particles to become active and by growth restriction due to a lower growth velocity and therefore less latent heat release [7,8].

The field of grain refinement has been extensively investigated for Al alloys over the past decades [2,3], resulting in the development of grain refiners, grain refining tests and furthermore in the development of several models to understand its
mechanism. In contrast, grain refinement of Cu alloys is less investigated. Grain refinement of Cu and Cu alloys seems to be of a complex mechanism that is strongly dependent on the alloy system under investigation, the solute concentration, the impurities and the casting conditions as well as the melt metallurgy. Therefore, it was suggested that Cu alloys have to be considered separately [9].

The objective of this work is to investigate the effect of solute content on the grain size in binary Cu alloys. The article reports both, accurately determined $Q$-values for the Cu-system using thermodynamic software tools and experimental results of the correlation between $Q$ and grain size in binary Cu alloys under defined cooling conditions of the TP-1 grain refiner test [10].

**EXPERIMENTAL PROCEDURE**

**Thermodynamic-based evaluation of $Q$**

The segregation power of alloying elements is expressed by the growth restriction factor $Q$ [11]:

$$Q = m(k - 1)c_0$$  \(1\)

where $m$ is the slope of the liquidus line, $k$ is the partition coefficient and $c_0$ is the solute concentration. These parameters can be derived from binary phase diagrams and were given by Cziegler et al. [12] and by Balart et al. [13]. However, the evaluation of $Q$ based on binary phase diagrams is strongly dependent on the resolution of the respective phase diagram [12]. To overcome the limitations of Eq. (1), $Q$ is suggested [11] to be evaluated as a calculation of the rate of development of the constitutional zone with respect to fraction solid at zero fraction solid:

$$Q = \left( \frac{\partial (\Delta T_{cs})}{\partial f_s} \right)_{f_s \to 0}$$  \(2\)

where $\Delta T_{cs}$ is the constitutional undercooling and $f_s$ the fraction solid. This can be derived from cooling calculations performed with thermodynamic software tools. In this work the software tools FactSage [14] and Thermo-Calc [15] were used based on a procedure given by Schmid-Fetzer and Kozlov [16]. With FactSage the calculations were performed under equilibrium cooling conditions for a temperature step of 0.1°C, which is the minimum temperature step provided by the software. With Thermo-Calc the calculations were performed under Gulliver-Scheil cooling conditions for a temperature step of 0.01°C, as at the beginning of the solidification $Q$ is independent of whether the solidification occurs under equilibrium conditions or not. Using data of temperature $T$ and the liquidus temperature $T_L$ given by the calculation results in the undercooling $\Delta T_{cs}$ [16]:

$$\Delta T_{cs} = T_L - T$$  \(3\)

To determine the rate of development of the constitutional zone with respect to fraction solid $f_s$, a second-order polynomial was fitted to 5 data points at $f_s \rightarrow 0$ (0 <
As a minimum temperature step of 0.1°C was used for FactSage, $f_s$ in the range $0 < f_s \leq 0.1$ was seen as valid:

$$\Delta T_{cs} = a + b * f_s + c * f_s^2$$  \hspace{1cm} (4)

The derivative of the second-order polynomial is given by:

$$\Delta T_{cs} = b + 2 * c * f_s$$  \hspace{1cm} (5)

At zero fraction solid $f_s$, $Q$ is directly given by [16]:

$$Q = b$$  \hspace{1cm} (6)

The $Q$-values of the alloying elements included in the database FSCopp [14] and TCCU1 [17] were calculated at 1 wt%. In the case that the maximum concentration of an alloy was < 1 wt% or that more than three data points were out of the range $0 < f_s \leq 0.01$ (Thermo-Calc), respectively $0 < f_s \leq 0.1$ (FactSage), $Q$ was calculated at a lower or higher concentration ($c_0$) of the alloying element and standardized at 1 wt%. The standardized $Q$-value can be given by [16]:

$$Q' = \frac{\partial Q}{\partial c_0}$$  \hspace{1cm} (7)

To obtain $Q'$, four more data points were calculated close to $c_0$. A second-order polynomial was fitted to five data points [16]:

$$Q = a + b * c_0 + c * c_0^2$$  \hspace{1cm} (8)

The derivative of Eq. (8) leads to the standardized $Q$-value for an alloying addition of 1 wt%:

$$Q' = b + 2 * c * c_0$$  \hspace{1cm} (9)

**Melt treatment procedure**

In order to test the correlation between growth restriction and grain size in Cu alloys, a set of Cu based alloys with single additions of Mg, P, Ti, Ni and Bi in the range up to 1 wt-% was prepared. Pure Cu (99.9 wt%) was used a base material. 2100g of pure Cu were charged in a clay-graphite crucible and remelted at 1250°C in an induction furnace. To avoid oxidation of the melt during the melting and holding step, the crucibles were covered with a graphite brick, sealed with fibrous material and the melting was under Ar atmosphere. After charging the base material and sealing the crucible the pure Cu was remelted at 1250°C +/- 5°C, hold for 1 minute before adding stoichiometrically calculated P as CuP15 for deoxidation due to a residual oxygen content of approximately 200 ppm in the base material. After the addition of CuP15, the melt was held for 1 minute for deoxidation before alloying was performed using commercially pure Cu-50Mg, Cu-15P, Cu-28Ti master alloys
and commercially pure Ni and Bi. After the alloying step the melt was held for 5 minutes at 1250°C +/- 5°C. Consecutively, the melt was poured into a preheated (316°C) graphite-coated TP-1 mould, followed by a rapid transfer to the TP-1 water quench, where the mould was left for 5 minutes. The cooling rate of 4 K s⁻¹ prior to the onset of solidification was determined using a type K thermocouple mounted at a height of 38 mm from the bottom surface in the centre of the TP-1 mould. The samples were sectioned horizontally at a height of 38 mm from the bottom surface. Standard metallographic procedure was applied to the samples and grain size was determined on the base of the line intercept method as per ASTM: E112-13 with at least 500 intersections per sample.

**Results and discussion**

**Growth restriction potency of alloying elements**

The results of the thermodynamic-based evaluation of the growth restriction potency of relevant alloying elements of the Cu-systems are shown in Table 1. The superscript * indicates that one or two data points are out of the range 0 < \( f_s \) ≤ 0.1 (FactSage), respectively 0 < \( f_s \) ≤ 0.01 (Thermo-Calc). These data points were not included in the polynomial fit. The subscript indicates \( c_0 \) used to evaluate the standardized \( Q' \). Small differences in the evaluated \( Q \)-values results mainly from the different temperature steps used in the calculation.

Nb as a peritectic forming element [18] was found to be the most powerful segregant in the Cu-system. However, the maximum concentration of 0.29 wt% [18] of Nb and therefore the limit growth restriction potency has to be considered. Further alloying elements with a high \( Q \) are Li and Mg. However, the high oxygen affinity [19] of these elements has to be considered, which applies also to further powerful segregants, e.g. P and elements with \( Q \)-values in the range of 10 K, e.g. Si, Zr. The reliable removal of oxygen prior to the alloying step of these elements must be facilitated. Oxygen itself shows a remarkably high \( Q \)-value and the grain refinement potency of oxygen in hypo-eutectic Cu-O alloys has been reported by Kobayashi et al. [20]. However, the susceptibility to H₂ embrittlement [21] has to be taken into account when melting at low oxygen concentrations. It is interestingly to note, that with the exception of Si the main alloying elements of Cu, e.g. Sn, Pb, Al, Zn show relatively low growth restriction potency. Nevertheless, the high amount of solutes in wrought and especially in cast Cu alloys can compensate to a degree.
Table 1. \( Q \) of relevant alloying elements of the Cu-system at a nominal composition of 1 wt% [22]. The superscript * indicates that one or two data points are out of the range \( 0 < f_s \leq 0.1 \) (FactSage), respectively \( 0 < f_s \leq 0.01 \) (Thermo-Calc) and were not included in the polynomial fit. The subscript indicates \( c_0 \) used to evaluate the standardized \( Q' \).

<table>
<thead>
<tr>
<th>Alloying element</th>
<th>( Q ) [K] (FactSage)</th>
<th>( Q ) [K] (Thermo-Calc)</th>
<th>Alloying element</th>
<th>( Q ) [K] (FactSage)</th>
<th>( Q ) [K] (Thermo-Calc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb</td>
<td>87.52 (0.1%)</td>
<td>84.70 (0.1%)</td>
<td>Sn</td>
<td>6.06</td>
<td>5.50</td>
</tr>
<tr>
<td>Li</td>
<td>47.89</td>
<td>-</td>
<td>Cd</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>38.02 (0.2%)</td>
<td>-</td>
<td>Sb</td>
<td>4.96</td>
<td>-</td>
</tr>
<tr>
<td>Mg</td>
<td>30.05</td>
<td>29.33</td>
<td>Mn</td>
<td>4.86</td>
<td>5.27</td>
</tr>
<tr>
<td>S</td>
<td>28.29 (0.5%)</td>
<td>-</td>
<td>Ni</td>
<td>3.52*</td>
<td>3.53*</td>
</tr>
<tr>
<td>P</td>
<td>23.48</td>
<td>27.03</td>
<td>Ag</td>
<td>3.51*</td>
<td>3.54*</td>
</tr>
<tr>
<td>B</td>
<td>-</td>
<td>19.58</td>
<td>Bi</td>
<td>3.49*</td>
<td>3.53*</td>
</tr>
<tr>
<td>Ca</td>
<td>18.43</td>
<td>21.43</td>
<td>Cr</td>
<td>3.45*</td>
<td>-</td>
</tr>
<tr>
<td>Si</td>
<td>11.28</td>
<td>9.53</td>
<td>Pb</td>
<td>2.59*</td>
<td>3.25*</td>
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<tr>
<td>Se</td>
<td>-</td>
<td>8.82</td>
<td>Al</td>
<td>1.61* (5%)</td>
<td>-</td>
</tr>
<tr>
<td>Ti</td>
<td>8.69</td>
<td>8.70</td>
<td>Co</td>
<td>1.26* (4%)</td>
<td>-</td>
</tr>
<tr>
<td>Zr</td>
<td>8.39</td>
<td>8.37</td>
<td>Fe</td>
<td>1.19* (2%)</td>
<td>-</td>
</tr>
<tr>
<td>Sr</td>
<td>8.37</td>
<td>-</td>
<td>Zn</td>
<td>1.03* (5%)</td>
<td>1.00 (5%)</td>
</tr>
<tr>
<td>As</td>
<td>6.67</td>
<td>7.47</td>
<td>Au</td>
<td>0.95* (20%)</td>
<td>0.91* (5%)</td>
</tr>
</tbody>
</table>

Influence of solute content on grain size in Cu alloys

The correlation between \( Q \) and grain size has been reported for Mg alloys [23] and for Al alloys [6]. To test the correlation between \( Q \) and grain size in Cu alloys, a series of Cu based alloys with five alloying elements with various \( Q \)-potency was prepared.

The results of the melting experiments under defined cooling conditions of the TP-1 grain refiner test are shown in Fig. 1(a)-(f). In Fig. 1(a)-(e) the average grain size is plotted against the nominal alloy composition in a range up to 1 wt%. Mg and P as the elements with the highest \( Q \)-value of the tested solutes decrease grain size at low alloy concentration. However, grain size significantly increases at higher P and in particular at higher Mg contents. Ti as an element with a significant lower \( Q \)-value compared to Mg and P shows similar results, as grain size decreases, but tremendously increases beyond a transition point. In contrast, Ni and Bi as the elements with the lowest \( Q \)-values lead to a continuously decreasing grain size to low levels.
Figure 1. Average grain size vs nominal solute content of (a) Mg, (b) P, (c) Ti, (d) Ni, (e) Bi, (f) average grain size vs $Q$.

The correlation between grain size and $Q$ is illustrated in Fig. 1(f), where the average grain size is plotted against $Q$ (values determined by Thermo-Calc). It is evident that a very limited correlation between the growth restriction potency of the alloying elements and the grain size was found for binary Cu alloys. Although grain size decreases with increasing $Q$ at low $Q$-values below 2K, the correlation between higher $Q$-values and grain size defers significantly from the correlation found for Al [6] or Mg [23] alloys. The elements with the expected lowest growth restriction potency Ni and Bi, respectively resulted in the lowest level of grain size. For elements with an assumed high growth restriction effect, Mg, P and Ti, respectively an increase in grain size was found beyond a transition point. Moreover, Mg and Ti reveal
excessive grain coarsening. Discrepancies between grain size and alloying elements at a solute concentration of 0.1 wt% have also been reported by Bustos [24]. Furthermore, equiaxed grain coarsening was observed in the work of Balart et al. [13] for several alloying elements. This raises the question which factors affect the low correlation between $Q$ and grain size in Cu alloys.

It has been reported that grain size in Al-Si alloys [23,25,26], as well as in Pb-Sb alloys [23] first decreases with increasing solute content and then increases beyond a transition point. Several suggestions have been given to explain this mechanism, such as decreasing solidification range, increasing superheat, increasing latent heat release [23], a change in growth morphology of crystals [26]. However, Lee et al. [23] suggested that a change in the nucleant potency distribution with increasing solute content might affect the transition in grain size, as fewer nucleants are activated. Therefore, the influence of the addition of the alloying element by affecting the nucleation potency of the melt has to be considered in this work. Equivalent to that, the influence of minor amounts of oxygen by both growth restriction and heterogeneous nucleation depending on the alloying element and/or further trace elements can be supposed. In a very preliminary study by this author [12] an interaction between the overall cooling rate influenced by the respective alloying element and $Q$ was suggested in Cu alloys. However, all these assumptions have to be submitted to detail investigation and further studies under defined casting conditions are required to determine the correlation between $Q$ and grain size in Cu alloys.

Conclusions

This work provides both, a comprehensive list of accurately determined $Q$-values for the alloying elements of the Cu-system and initial experimental results under defined cooling conditions of the TP-1 grain refiner test with regard to the correlation between grain size and growth restriction in binary Cu alloys. However, initial experimental results show a low correlation between $Q$ and grain size in binary Cu alloys, which requires further detail investigation.

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References


