On the Nature of Cell Boundaries in Rapidly Cast Al-Alloys

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The impurity cell structure of rapidly cast Al-Si, Al-Mg and Al-Ag alloys is investigated with respect to the occurrence of second phase and dislocations as a function of solute concentration. Considering the dislocation arrangement, three types of cell boundaries corresponding to various concentration ranges could be distinguished. Comparison of the three alloys leads to the conclusion that the dislocations are introduced by constitutional stresses, which depend only on the severity of segregation and the difference in atomic size between solvent and solute atoms.

I. Introduction

A recent report(1) dealt with preliminary structural observations on rapidly solidified Al-foils containing 0.1-0.2% Si. The microstructure of this material consisted of large grains subdivided by an irregular network of cell boundaries, as it is usually found in rapid castings of Al(2)-(4). Electron microscopic observations showed that these cell boundaries contain a dense array of tangled dislocations and precipitates. The latter are preferably located at nodal points. In an extension of this work the present paper intends to: a) demonstrate various effects of solute concentration on the character of the cell boundaries in the Al-Si system; b) to elucidate the influence of second phase particles and constitutional stresses(5)(6) on the appearance of the tangled dislocation arrays at the cell boundaries by comparing the results of Al-Si alloys with those on Al-Mg and Al-Ag alloys cast under similar conditions. Since both Mg and Ag have high solubility in Al, second phase is formed only at comparably high concentrations. However, the atomic radius of Ag (1.44 Å) is near that of Al (1.43 Å), while that of Mg (1.60 Å) is appreciably larger. It will be shown that the constitutional stresses, caused by segregation of the alloying element at the cell boundaries and by the difference in atomic radius between the solute and the matrix element(5) are the most probable origin of the dislocations.

II. Experimental Procedure

The alloys investigated are listed in Table 1 and Table 2. The Al-Si and Al-Mg alloys used were prepared from 99.999% Al and a master alloy, while

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(2) M. Smialowski: Z. Metallk., 29 (1937), 133.
structure similar to that described in the literature (7) and (8). These surface structures were removed by electrolytic polishing in a 1:6 hydroperchloric alcohol mixture. Subsequently the specimens were thinned by the standard window method for observation at 100 kV in a JEM-6A electron microscope. The typical character of each feature observed was ascertained by the investigation of 10~20 electron microscopic specimens for each alloy.

Specimens for optical microscopic observation were electrolytically prepolished and etched with Keller's etchant to reveal the segregation cell structure. Etching with a 1% HF aqueous solution or a 10% NaOH solution gave the same results. Furthermore the specimens observed in the electron microscope were mounted on a microscope slide and again investigated in the optical microscope. In some cases the regions of electron microscopic observation could be identified from the contamination caused by the electron beam.

Electron probe microanalysis was employed to obtain some information on microsegregation. Line scanning was performed with a Shimazu Microanalyzer operated at 15 kV and 0.3 μA specimen current. The diameter of the electron beam was about 3~4 μm.

III. Experimental Results

1. Optical microscopic observations

Photo. 1 shows the cell structure which exists within the grains of Al-Si alloys. In the base metal and the Al-0.01 Si alloy the cells have regular hexagonal or elongated shapes depending on the grain orientation. In the Al-0.05 Si alloy the transition to cellular dendrites is recognized in the branches, which extend into the interior of the cells. Small regular cells were found only near the grain boundaries. In the higher concentration alloys only a cellular dendritic structure as described already(1) occurred, whereby increasing Si concentration increased the frequency of dendritic branching. In the Al-1.2 Si alloy an extensive formation of the second phase took place along the cell boundaries. It may be noted, however, that in the Al-Mg alloys very strong etching was locally observed. As the electron microscopic observations showed that no second phase occurred, this phenomenon indicates an

inhomogeneous distribution of the solute along the boundaries.

The change from regular to dendritic cell structures in the Al-Si and Al-Mg alloys was accompanied by an increase in grain size from about 0.1~0.5 mm to several millimeters and a change of the etching behaviour. Prolonged etching lasting for 15~20 minutes at room temperature was necessary in the purer alloys, where the intensity of etching varied with different grains. On the other hand, etching for 30 to 60 seconds was sufficient in the higher alloyed materials to produce a good contrast of the cell boundaries as shown in Photos. 1 and 2. In all materials, however, preferential etching of the cell boundaries was observed. As already mentioned, this effect was especially pronounced in the Al-Mg alloys.

Tables 1 and 2 show the cell sizes of all materials, measured by a method proposed by Kostron(3). In general the cell sizes of all three alloys were of the same order of magnitude. Finally it is evident from these tables that the cell sizes measured from the optical and electron micrographs coincide well with each other. This ascertains that the same structure was investigated in both cases.

2. Electron microscopic observations

(1) Al-Si

In general the addition of an alloying element had a strong influence on the appearance of the cell boundaries with respect to the dislocation and second phase distribution. In particular the Al-Si system showed three different types of cell boundaries, which correspond to low, medium and high Si concentrations.

Below 0.05% Si only grain boundaries and individual isolated dislocations were observed in the electron microscope, but no dislocation arrangement was found which could be correlated to the cell structure of Photo. 1(a). Furthermore no second phase was detected. Photo. 3 shows an optical micrograph of a part of a foil; the same area was also investigated in the electron microscope and subsequently slightly etched. At the locations of electron microscopic observation, which can easily be recognized at the foil edge, the cell structure and two grain boundaries are clearly revealed, while in the electron microscope only the grain boundaries were detected. Therefore, the cell structure may be interpreted to consist of plain segregation boundaries, at which the alloying element is enriched but does not introduce any lattice defects.

The Al-0.05 Si and Al-0.1 Si alloys show cell boundaries, which contain dislocations and second phase particles as described previously(1) (Photo. 4). In this case, as the Si concentration became higher, the dislocation density increased. The orientation difference across the boundaries was in the order of a few minutes. In Photo. 4(b), which shows a cell boundary steeply inclined to the foil surface, the tangled dislocation arrangement forming an irregular three-dimensional array is clearly recognized. However, from boundaries which were oriented nearly parallel to the electron beam it was established that the width of the dislocation arrays was less than one micron. It is noted that the transition from plain segregation boundaries to those containing dislocation arrays coincides with the change in the optical microstructure and the etching behaviour described in section III-1.
Together with the dislocations the second phase appeared at the cell boundaries. Their nature could not be established from the electron diffraction patterns, but the purity of the two phase alloy and electron microprobe analysis of nodal points suggested strongly that they consisted of essentially pure Si.

Two types of second phase particles, which formed at nodal points and along the cell boundaries respectively, could be distinguished, and their average sizes are given in Table 3. At the nodal points large globular particles formed as described by Obinata et al. An example of a nodal point in Al-0.05 Si is given in Photo. 5. It is seen that these particles are surrounded by dislocations which according to their form and arrangement seem to have originated from dislocation loops nucleated at the particle during cooling. As these particles were found at all nodal points, their distance in the normal direction of the foil can be assumed to be in the order of the electron microscopic foil thickness of 0.2~0.3μ, which is also equal to the average particle diameter given in Table 3. Therefore, the nodal particles are very closely spaced in the direction, which is the growing direction, in accordance with the findings of other authors. This is also indicated by the presence of two or more particles at some of the nodal points. It can be readily shown that during a cooling time of approximately 1 sec, during which the foil reaches the temperature of 400°C after casting, a Si concentration near that of the eutectic point would be required to produce a string of such large particles by precipitation from the solid. It is therefore concluded that the second phase at the nodal points is formed at the moment of solidification by disintegration of a small channel of the highly enriched rest melt.

The second phase, which was found along the cell boundaries, consists of small globular particles interspersed in the dislocation tangles as shown in Photo. 4(b). These particles consistently seem to have nucleated at the dislocations of the cell boundaries and can therefore be considered as precipitates formed during cooling after solidification. The globular shape indicates that precipitation must have occurred in the high temperature region. As the solubility of Si in Al increases rapidly with temperature, it can be concluded that a solute enrichment to about 1% Si at the cell boundaries preceded the precipitate formation.

The appearance of typical cell boundaries at more than 0.3% Si addition is illustrated in Photo. 6. The most striking feature is the absence of any tangled dislocation arrays along the cell boundaries. Instead a subboundary-like image is observed, exhibiting either thickness contours or, under appropriate diffraction conditions, regular two-dimensional dislocation networks. The orientation difference across

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Table 3 Average size of second phase particles in Al-Si alloys

<table>
<thead>
<tr>
<th>Material</th>
<th>Second phase diameter</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cell node</td>
</tr>
<tr>
<td>Al-0.05 Si</td>
<td>0.05μ</td>
</tr>
<tr>
<td>Al-0.1 Si</td>
<td>0.27μ</td>
</tr>
</tbody>
</table>

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the cell boundaries was usually in the order of one degree for both the Al-0.3 Si and the Al-1.2 Si specimens.

As expected from the increased Si concentration, the second phase appeared abundantly along the cell boundaries in Al-0.3 Si and Al-1.2 Si. (Photo. 6). The precipitation of Si occurred either in the form of globulus or in continuous platelike layers lying in the cell boundary. A new form of the second phase appearance was observed at nodal points in Al-0.3 Si and along many boundaries in Al-1.2 Si. As illustrated in Photo. 7 it consists of a fine dispersion of small particles with a size of about 0.1μ. Selected area diffraction from such boundaries yielded ring patterns of the Si phase, with no indication of a preferred orientation. As these finely dispersed particles occur only at the highest concentration, it seems likely that they constitute a special way of decomposition of the eutectic rest melt. In splat cooled eutectic Al-Si alloys similar small silicon particles in random orientations were observed(11).

(2) Al-Ag and Al-Mg

In order to evaluate the general validity of the foregoing results and to elucidate the influence of the second phase on the nature of the cell boundaries, similar investigations were performed on specimens of the Al-Ag and Al-Mg systems. As these two systems show a high solubility compared to the Al-Si system no primary second phase was observed at cell boundaries in the alloys investigated (see Table 2). Only in the Al-3 Mg alloy a larger particle (probably of the β-phase) was occasionally detected at nodal points. The shape and size of these particles were similar to those at the nodal points of the Al-Si alloy as shown in Photo. 5.

With respect to the dislocation structure at the cell boundaries, no singular features were observed, but neither Al-Ag nor Al-Mg alloys showed all three boundary types found in Al-Si.

In the Al-Ag alloys containing up to 4% Ag (=1 at% Ag) only plain segregation boundaries existed. In no case a dislocation arrangement could be correlated to the cell boundaries, which usually were visible in the electron microscope due to preferential polishing during the specimen preparation (Photo. 8). Isolated stray dislocations were the only feature occasionally observed. As the optical micrographs of these alloys showed distinctly a cellular dendritic growth, similar to the high-concentrated Al-Si alloys, it has to be concluded that the dendritic growth alone is not a sufficient criterion for the appearance of dislocation.

tangles at cell boundaries in Al-alloys.

The Al-Mg alloys exhibited plain segregation boundaries at a concentration below 0.5% Mg. At higher concentrations dislocation arrays appeared first at and near cell boundary nodes (Al-0.5 Mg) and then also along the cell boundaries (≥1% Mg). The transition from plain segregation boundaries to those containing dislocations was again associated with a change in the optical microstructure and etching behavior as described earlier.

Photo. 9 shows a cell in a Al-1 Mg, specimen, which is also typical for the Al-3 Mg alloys. Again areas of tangled dislocations outline the cell boundaries. Note, however, that, while in Al-Si alloys the dislocation density was fairly uniform along the boundaries, in this case locations of higher dislocation densities are connected by boundary segments where fewer dislocations exist. The areas of high dislocation density can be correlated to the locally strong etching attack described in section III-(2) and therefore seem to be connected with the locally high solute segregation. This is also confirmed by the observation that only at those locations small precipitates nucleated at the dislocations in the Al-3 Mg alloy. The absence of a primary second phase in Al-Mg alloys establishes that second phase particles cannot be the cause of the tangled dislocation arrays along cell boundaries in Al-alloys.

The third type of boundary reported for Al-Si alloys was not found in the other two alloy systems. Even in a specimen containing 10% Mg the second phase still occurred as large globular particles at nodal points only, while the dislocation structure still formed irregular arrays. It cannot be decided whether the third boundary type is connected with extensive eutectic decomposition along cell boundaries, or is a feature peculiar to high-concentrated Al-Si alloys.

### 3. Electron microanalysis

To obtain some information about the segregation of solute at the cell boundaries, microanalysis was performed on samples of Al-0.1 Si, Al-1 Mg and Al-1 Ag alloys. The specimen was moved at a constant rate so that the probe beam transversed the boundaries of a typical structure as shown in Photos. 1 and 2. As the diameter of the electron beam of the microanalyzer was about 3~4μ, and as in light element materials the area contributing X-rays to the analyzing counter is larger than the beam diameter(12), no quantitative results could be expected. Especially it is impossible to determine the solute concentration at the boundary itself, as the electron micrographs indicate a boundary width of less than 1μ. Investigation was therefore limited to demonstrate the existence of segregation.

In Al-Si alloys the solute concentration was too low to give any indication of segregation, as the readings of the microanalyzer stayed at the background level. The existence of strong segregation even in the Al-0.05 Si alloy is proved, however, by the appearance of the second phase particles and precipitates.

Microanalysis traces for Al-Mg and Al-Ag alloys are given in Figs. 1(a) and (b). Note that the distance of the peaks corresponds approximately to the cell size given in Table 2. Due to the small cell size in the Al-1 Mg alloy the peaks corresponding to boundaries frequently overlapped. The width of the peaks can be considered to reflect the width of the beam and to a certain extent the inclination of the boundary to the specimen surface. In both cases the peak readings are twice those of the cell interior, but the actual segregation seems to be much higher.

It is therefore concluded that extensive segregation occurs at the cell boundaries in all three alloys.

### IV. Discussion

From the foregoing observations it is concluded that in principle three types of cell boundaries can be distinguished in rapidly solidified Al-alloys according to the presence and arrangement of dislocations:

I. Plain segregation boundaries, containing no dislocations
II. Cell boundaries containing an array of tangled dislocations
III. Cell boundaries containing two dimensional regular dislocation networks.

All three types of boundaries exhibit solute segregation. The appearance of the second phase along the boundaries is a function of the severity of segregation and of maximum solubility. The following discussion is centered around the boundaries of type II:

Various mechanisms have been proposed for the occurrence of dislocations in solidified metals (e.g.(13)):

1. Propagation of dislocations nucleated at a mould wall
2. Collapsing of vacancy discs
3. Internal shear stresses, which arise from thermal strains or mechanical constraints during cooling
4. Local stresses at impurity or second phase particles

(5) Dendritic growth, resulting in slight misorientations or thermal fluctuations
(6) Constitutional stresses arising from abrupt composition changes and the resulting changes in lattice parameter.

Evaluating the possibility of any such mechanisms to explain the present results, the first three processes may be excluded, as it is difficult to see how dislocations produced in such ways should arrange themselves along the cell walls. Instead they would be expected to produce either large regular subboundaries as a result of polygonization (as the striation structure in single crystals) or “cell walls” typical for deformed materials, the size of which is much smaller than the observed impurity structures. Furthermore these three mechanisms are independent of the solute concentration, and it appears from the results that the solute addition is a necessary though not a sufficient condition for type II boundaries. Mechanism 4 was shown to be operative at larger second phase particles (Photo. 5). But while this may result in an increased dislocation density in the vicinity of the particles, it cannot explain dislocation arrays along boundaries which stretch up to 10μ between the locations of the second phase. Furthermore in Al-Mg alloys dislocation arrays appeared although the second phase was absent. Dendritic growth also cannot play a dominant role as in Al-Ag alloys dendritic growth causes no dislocation arrays.

The last mechanism, however, seems to be capable to account for all observations. In the theory of constitutional stresses developed by Goss et al.\(^(5)\) and Tiller\(^(6)\) it is shown that a rapid change of concentration \(dC\), which is accompanied by a corresponding change in lattice parameter \(da=\Delta C (da/dC)\), brings about stresses which may be relieved by dislocations. The number of dislocations is given by

\[
\eta = \Delta C \left( \frac{da}{dC} \right) \frac{1}{a_b}
\]

\((b=\text{Burgers vector})\)

if it is assumed that the concentration change occurs stepwise and the total stress is relieved by dislocations. In dendritic solidification it was shown\(^(14)\) that the solute concentration increases steeply only near the end of solidification justifying the first assumption, while the second one clearly overestimates the dislocation density. A qualitative discussion of eq. (1) with respect to the present results is not possible, as the concentration difference between the cell interior and boundary is unknown. It may be assumed, however, that for similar solidification conditions the segregation in dendritic growth is mostly determined by the equilibrium distribution coefficient \(k_0\). From the values for \(k_0\), which are given in Table 4 and from the results of the qualitative micro-analysis described in section III-3, it may be assumed that \(dC\) is a large positive number for all three systems, being perhaps similar for Al-Ag and Al-Mg alloys. Then second important factor of eq. (1), \(da/dC\), is also given in Table 4, indicating nearly zero constitutional stresses for Al-Ag alloys and therefore no boundary dislocations in accordance with the experiments, while in Al-Mg alloys a higher value for \(da/dC\) may compensate for a higher \(k_0\) compared to Al-Si alloys. In fact, similar dislocation structures were found in these two alloys.

### Table 4 Distribution coefficient and the change of the Al-lattice parameter with solute content for the Al-alloys investigated

<table>
<thead>
<tr>
<th>Material</th>
<th>(k_0)</th>
<th>(da/dC) (Å/ at%(C))</th>
<th>Expected dislocation density</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-0.1 Si</td>
<td>0.14</td>
<td>0.0020</td>
<td>high</td>
</tr>
<tr>
<td>Al-1 Ag</td>
<td>0.3</td>
<td>very small</td>
<td>very low</td>
</tr>
<tr>
<td>Al-1 Mg</td>
<td>0.3</td>
<td>0.0048</td>
<td>high</td>
</tr>
</tbody>
</table>

The transition of type I to type II boundaries would require an increased severity of segregation, which corresponds in Al-Si and Al-Mg alloys with a transition to cellular dendritic growth. This assumption seems probable in the light of the changed etching behaviour described in section III-1, which is not caused by the presence of dislocations as shown on the example of the Al-Ag alloy.

In an ideal case the dislocations introduced by the constitutional stresses would form a regular cross grid in the planes at which the concentration changes occur. The tangled dislocation arrays found can, however, be explained by climb movements during cooling after solidification.

Nothing can be deduced from the present results about the causes leading to cell boundaries of type III. Although they seem to be connected with the severe distortions, an extensive formation of eutectic along the cell boundaries may cause, investigation of other alloy systems will be required to elucidate this point.

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\(^{(14)}\) M. C. Flemings : Modern Casting, 64 (1964), 353.
V. Summary

From the results of this paper and the discussion it may be concluded that the types of cell boundaries and their corresponding features depend on the alloy system as follows:

Type I: is a plain segregation boundary, at which the alloy addition is enriched but still remains in solid solution. No special structural defects are observed at such boundaries. They occur at low values of segregation and/or a small change in lattice parameter with solute concentration \((\text{d}a/\text{d}C)\).

Type II: is characterized by arrays of tangled dislocations. Second phase particles may occur as well, especially at nodal points. The dislocation density depends on the severity of segregation and on the value of \(\text{d}a/\text{d}C\). Appearance of a second phase depends on the severity of segregation and the maximum solubility at the eutectic temperature.

Type III: is characterized by regular dislocation networks. It was observed to be connected with the formation of eutectic along the boundaries but the true reason of its origin is not well understood.

It is suggested that this classification gives a further insight into the boundary nature than the conventional one, which is based on the appearance of eutectic alone\(^3\). As no special assumptions were made with respect to the alloy system, the results should have general application. To prove this point, however, investigation of other alloy systems with widely different characteristics would be required.

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