Control of Shape of Faceted Crystal Solidified in Cast Alloys

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ABSTRACT

A variety of shapes of primary faceted crystals solidified directly from the melt are observed in different cast alloys. These crystals may have metallic, covalent or ionic atomic bonds. Shape modification of primary solidified faceted phases is an important tool for improvement of properties of cast alloys. In this article, the different methods were experimentally tested to change the shape of primary faceted crystals in multi-components Al- and Fe-based alloys. The investigated methods changed the shape of primary crystals by controlling nucleation and growth conditions and included:

- melt inoculation for enhancing heterogeneous nucleation;
- shearing mushy zone to control thermal and constitutional undercooling on solidification front;
- micro-alloying additions for changing the electronic properties of solidified phases.

The thermodynamic simulation and a hypothesis, which described the mechanism of shape modification of the crystals with covalent atomic bonds by donor elements, were used to design melt treatment. The achieved structural changes were analyzed using optical microscopy, SEM, and TEM. The possible mechanisms of shape control of solidified faceted crystals in cast alloys are discussed.

Keywords: solidification, phase shape modification, aluminum alloys, austenitic steel

1. INTRODUCTION

Cast multi-component alloys have a heterogeneous structure consisting of a main metallic phase along with the other phases having metallic, covalent or ionic atomic bonds. The terms “sharp”, “smooth” or “faceted” and “rough”, “continuous”, “diffuse” or “non-faceted” are interchangeably used in literature to characterize two basic types of crystal interface. The terms faceted and non-faceted will be used in this article to characterize the two types of interfaces. Typically, a primary metallic phase (e.g. α-Al in aluminum alloy or Fe-FCC in austenitic Cr-Ni stainless steel) solidifies as a non-faceted dendrite with an atomically rough surface, while directly precipitated from the melt intermetallic, covalent phases and compounds with ionic bonds form different elongated faceted shapes (plate, polyhedron, needles, faceted dendrites) with atomically flat surfaces. For example in hypoeutectic Al-Si alloys, primary not-faceted α-Al phase has metallic atomic bonds and conductive electrons, while the faceted Si-phase, formed during eutectic reaction or as a primary phase in hypereutectic alloys, is a typical semiconductor with covalent atomic bonds. A similar difference in electronic properties and type of atomic bonding can be observed in phases formed in hypereutectic Al-Ge, Al-Si-Mg, Mg-Si, and Al-Sb alloys containing Ge, Mg, Si or AlSb covalent crystals. Primary faceted phase also observed in Fe-based alloys. Cast iron with flake graphite is a typical example of such heterogeneous alloy. Cast steels have more homogenous structure; however primary intermetallic compounds such as carbides and nitrides of transitional metals (Ti, Nb, Hf) also precipitated as faceted crystals in these alloy. Fig. 1 illustrates different faceted angular elongated (not compact) phases observed in technical alloys. Unfortunately, unmodified alloys with such large faceted crystals have low ductility and strength because these brittle formations can easily be broken.
Gibbs-Curie-Wulff’s theorem predicts the equilibrium polyhedron shape of solidified phases having anisotropy of surface energy based on the fundamental thermodynamic principle of Gibbs energy ($\Delta G$) minimization [1]:

$$\frac{\sigma_1}{h_1} = \frac{\sigma_2}{h_2} = \cdots \frac{\sigma_i}{h_i}$$  \hspace{1cm} (1)

where: $\sigma_i$ is the surface energy of face “i” and $h_i$ is a distance from a common point to a face.

However, this theorem cannot predict roughness of atomic surface of solidified crystal. To predict surface atomic topology of solidified crystals, Jackson [2] analyzed the change of Gibbs energy during the growth of crystal with different melting entropy ($\Delta S_{sol}$). The Jackson’s hypothesis did not consider any limitations to delivery atoms from the melt to solid–liquid interface. In this condition, two types of surfaces with the different relative numbers of occupied atomic positions on the growing surface ($N_i/N$) were predicted. The first one is an atomically flat interface, faceted at the atomic scale ($N_i/N \rightarrow 0$ or 1), and the second one is an atomically rough interface, non-faceted at the atomic scale ($N_i/N \rightarrow 0.5$). The first type is inherent to crystals with ionic and covalent atomic bonds having a high melting entropy $\Delta S_{sol} = L/T_{sol} > 16$ J/g-mol K. Metals having a low melting entropy $\Delta S_{sol} < 16$ J/g-mol K solidify in the shape of dendrites with curvilinear non-faceted surfaces.

The magnitude of $\Delta S_{sol}$ is determined by changing the atomic and electron states during solidification from disorder of atoms and electrons in a metallic liquid to different degrees of order in the solid state. Regel and Glazov [3] considered the following three components of the total value of melting entropy:

- positional ($\Delta S_{pos}$), determined by disorder-order transformation of atoms;
- oscillational ($\Delta S_{os}$), related to atom oscillation frequency;
- electronic ($\Delta S_{el}$), determined by difference in electron states in melt and crystals.

The total value of melting entropy during solidification of the metallic phase is only determined by the change of atomic order and oscillation frequency, i.e. $\Delta S_{pos} + \Delta S_{os}$, which equals 8-12 J/g-mol K. However, during solidification of a phase with covalent atomic bonds, both atomic and electron disorder-order transformations take place. As a result, the total value of the melting entropy increases by $\Delta S_{el}$ (Table 1). For example in Al-Si alloys, the value of latent heat of Si-phase is 4 times greater than that of $\alpha$-Al. Precipitation of graphite phase also increases latent heat of Fe-C alloy. It was suggested [2] that such difference in melting entropy of metallic, intermetallic and covalent primary precipitates influences the atomic surface topology of solidified phases in casting alloys. Metallic type phases solidify when atoms settled easily to any point of the surface with formation of a non-faceted interface. On the other hand, phases with covalent and ionic bonds solidify as faceted angular crystals.
Table 1. Components of melting entropy and latent heat [3].

<table>
<thead>
<tr>
<th>Materials</th>
<th>Components of melting entropy (J/g-mol K)</th>
<th>Latent heat, J/g</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\Delta S_{pos}$</td>
<td>$\Delta S_{os}$</td>
</tr>
<tr>
<td>Metals:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>10.9</td>
<td>0.4</td>
</tr>
<tr>
<td>Cu</td>
<td>9.7</td>
<td>0.4</td>
</tr>
<tr>
<td>Fe</td>
<td>8.0</td>
<td>0.4</td>
</tr>
<tr>
<td>Covalent phases:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>1.7</td>
<td>6.7</td>
</tr>
<tr>
<td>Ge</td>
<td>3.8</td>
<td>4.6</td>
</tr>
<tr>
<td>AlSb</td>
<td>4.2</td>
<td>12.6</td>
</tr>
<tr>
<td>Mg$_2$Si</td>
<td>8.4</td>
<td>16.8</td>
</tr>
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</table>

Jackson’s hypothesis is based on thermodynamic assumptions and it is helpful for first selection of micro-alloying additions for shape modification based on analysis of electronic properties. However, this hypothesis did not consider the possible effects of kinetic limitations. Cahn developed a more detailed explanation for faceted or non-faceted solidification modes including the melt undercooling effect [1]. Cahn’s model predicts lateral growth faceted interface at low undercooling and a transition at critical undercooling from lateral to continuous growth with non-faceted interface. The critical questions about the unique criterion for faceted/non-faceted growth transition in a specific alloy and the effects of impurities remain unsolved.

The nucleated small crystals have a near equilibrium shape predicted by Gibbs-Curie-Wullf’s theorem and surface topology followed by Jackson’s or Cahn’s models; however, the instabilities of freely growing interfaces produce morphological evolution of the shape. The factors that lead to shape instability include: (i) surface energy of a curved interface, (ii) attachment kinetics of atoms, (iii) trapping of solute elements, (iv) mass transport of alloying elements, and finally, (v) possible constrained growth at the end of solidification. Because of these disturbances, the solidified crystal begins to develop a complex dendritic shape, growing in a kinetically preferred crystallographic direction. Consequently, at low anisotropy of the solid-liquid interfacial energy in metallic phases, the developed non-faceted dendrites exhibit large radius of tip, while covalent and ionic phases with high anisotropy of the solid-liquid interfacial energy will exhibit sharp faceted morphology.

Considering these theoretical models, control of the primary crystal shape in solidified in technical alloys could be done using different technological approaches, which may be divided into two main groups (Fig. 2).

Fig. 2. Map of methods used for shape modification of primary phases formed during solidification.
The group of physical methods modifies structure by applying mechanical (vibration, pressure, centrifugal forces or vacuum), thermal (cooling rate or thermal gradient) or electro-magnetic forces which change nucleation and growth conditions of primary phases. This group of methods can produce self-nucleation effect by broken dendrites of primary phase. Physical methods also can be used for control of phase growth by influencing on interfacial and near field phenomena, such as constitutional undercooling. In this article, a combination of alloying and shearing of semisolid aluminum alloy was tested to control the shape of primary Fe-Si-Mn phase which has negative effect on properties of iron contaminated secondary alloys.

The second group includes chemical methods which modify the cast structure with the addition of a small quantity of active elements (Fig. 2). The special additions could be added to simultaneously control nucleation and growth through the different mechanisms. The possibility of chemical modification of the shape of primary phases with covalent atomic bonds was discovered in a number of alloys. For example, Na or P additions modify the shape of the primary Si-phase in hypereutectic Al-Si alloys [5]. Chemical modification of the shape and size of the primary Mg2Si phase solidified in hypereutectic Al-Mg-Si- and Mg-Si-alloys has been described [6,7]. Magnesium [8] and cerium [9] modify flake graphite to spherical graphite in cast irons.

Discussion concerning the shape phase transformation phenomenon continues from the time of first discovery. According to solidification theory, all suggested hypotheses can be divided into two main groups. The first group of hypotheses describes the shape phase modification effect through the influence of small element additions on the heterogeneous nucleation process. For example, AlP particles were discovered inside the primary silicon crystals formed in hypereutectic Al-Si alloys modified by phosphorus [10]. Magnesium and calcium oxides along with sulfide substrates were found in the center of spherical graphite in ductile iron [11-13]. The active heterogeneous nuclei for alloy solidification can be formed in the melt by the chemical reactions between the modifier additions and the elements dissolved in the melt. Heterogeneous nucleation decreases the nucleation energy barrier and reduces the melt undercooling for phase precipitation. Crystallographic coherency and similarity between the substrate and the nucleated solid phase increases heterogeneous nucleation efficiency. Effective heterogeneous nucleation increases the crystal population density and decreases crystal size. The restricted domain for crystal development in the melt could influence on the shape of primary precipitate while the effect on faceted surface topology could be minimal.

There others mechanisms also could be involved in shape modification. For example, Na- and Sr-additions modify Si-phase in Al-Si alloys and both these elements increase the melt undercooling before forming Al-Si eutectic. Cast iron with spherical graphite also has a significantly higher undercooling after Mg treatment in comparison to unmodified iron with flake graphite. These experimental data reveal that heterogeneous nucleation is not the only controlling mechanism in shape phase modification, since shape transformation can also be a result of altering crystal growth by the other different mechanisms (Fig. 2). The influence of small modifier additions on the growth of primary crystals and eutectic phases were described through selective surface absorption [14, 15]. The eutectic microstructures modified by Na- and Sr- alloys exhibit a fine fibrous morphology in comparison with the coarse flake type eutectic morphology of unmodified Al-Si alloys. Crystallographic studies using high resolution transmission electron microscopy have shown that impurity modification results in an enormous increase in twin density in the eutectic Si when compared with unmodified eutectic Si. The modifier atoms, such as Na and Sr, could develop impurity buildup in front of the growing silicon crystals [16, 17]. The changes in selective surface absorption of S and O produced by Mg additions into the iron melts were considered a factor dominated in graphite shape modification [18].

It is interesting to note, that the role of surface-active impurities have been described in aluminum and iron alloys from different points of view. In aluminum alloys, surface-active impurities (Na, Sr) are considered to be blocking elements which can develop effective impurity buildup in front of Si growth. On the
In this article, several methods of shape modification of primary faceted crystals with additions which enhance heterogeneous nucleation and change electronic structure of growing phases by donor type impurity were investigated in iron and aluminum alloys. The location of the studied methods in a map of the different chemical and physical methods is shown in Fig. 2.

2. EXPERIMENTAL DESIGN AND RESULTS

2.1 Modification Nb(CN) in Fe-Cr-Ni-Nb alloy by enhancing heterogeneous nucleation

Hypothesis and experimental design. Austenitic Cr-Ni steels alloyed by Nb are used industry for multiple high temperature applications (heat exchangers, automotive turbochargers). However, elongated plate-like primary Nb(CN) negatively affected on ductility. Stimulation of heterogeneous nucleation will increase the number of crystals per unit volume. Because small crystals will experience less instability during free growing in the melt, stimulation of heterogeneous nucleation can modify their shape. The classical analysis of the heterogeneous nucleation activity of a “foreign” solid in the melt predicts favorable conditions for nucleation at the low wetting angle [20]. Bramfitt [21] modified the Turnbull-Vonnegut equation to calculate the two-dimensional planar disregistry for characterization of the precipitate capability to serve as heterogeneous nucleation sites. The authors performed ab initio calculations of lattice parameters of carbides and nitrides of transitional metals [22] which can be formed in austenitic steels [23]. Titanium and niobium carbo-nitrides have similar atomic structures and lattice parameters with disregistry less than 5%, so they can be easy nucleate each other in iron melt.

FactSage thermodynamic software [24] was used to simulate solidification sequence in the base and experimental stainless steels (Table 2). A base steel was designed to have a primary faceted niobium carbo-nitride phase. A modified steel was designed to cause titanium nitrides to be precipitated from the melt first and this compound could then serve as a nucleation site for niobium carbo-nitrides upon melt cooling (Fig. 3). Thermodynamic simulation also predicts some mutual solubility of Nb in titanium nitride and Ti in niobium carbides, as well as mutual solubility of carbides and nitrides of these transitional metals. It could help decreasing nucleation barrier. Two experimental heats were performed in a 100 lbs induction furnace and steels were poured into a no-bake sand mold. Casting plates had 0.75” wall thickness. SEM/EDX analysis was performed using ASPEX PICA system (FEI Hillsboro, OR, USA). For detailed examination of the precipitates, TEM studies were performed using TEM/STEM Tecnai F20 (FEI Hillsboro, OR, USA). The TEM specimen was cut using dual beam Helios Nano Lab 600 (FEI Hillsboro, OR, USA).

Table 2. Composition of base and modified experimental austenitic stainless steels (wt. %).

<table>
<thead>
<tr>
<th>Steel</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Cr</th>
<th>Nb</th>
<th>Ni</th>
<th>N</th>
<th>Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base</td>
<td>0.5</td>
<td>1.2</td>
<td>1</td>
<td>20</td>
<td>2</td>
<td>15</td>
<td>0.1</td>
<td>-</td>
</tr>
<tr>
<td>Modified</td>
<td>0.5</td>
<td>1.2</td>
<td>1</td>
<td>20</td>
<td>2</td>
<td>15</td>
<td>0.1</td>
<td>0.5</td>
</tr>
</tbody>
</table>
**Experimental results.** SEM images (back scattered electron detector) of a base and a modified austenitic steels are shown in Fig. 4. A base case steel has plate-like faceted niobium carbo-nitride crystals (white phase in Fig. 4a). The addition of titanium changed the shape of the primary niobium containing phase, making it into small faceted compact crystals (Fig. 4b). The titanium bearing (dark) crystals, which could presumably be heterogeneous nuclei of the niobium-bearing phase, are present on the center of the white niobium-bearing phase (Fig. 4c). The EDX chemistries obtained from the white and black phases are given on Fig. 4c.

![Fig. 4. SEM images of base (a) and modified (b, c) stainless steels. EDX results (wt. %) shown in (c).](image)

To examine the structure and phases in more detail, a TEM sample was cut from a complex precipitate in a modified steel using the focused ion beam. The boundary between the two phases appeared relatively flat at high TEM magnification. A high resolution EDS line scan (approximately 10 nm step and 10 nm spot sizes) was taken from a titanium bearing core to a niobium faceted crystal (Fig. 5a). Although the line scan was performed at high resolution, some overlap was observed between the various phases at that particular sample orientation, creating somewhat indistinct phase boundaries (Fig. 5b). The lattice orientation relationships among these two phases were defined from the overlap zone (Fig. 5c,d). At the particular sample tilt used, the core TiN phase was found to be almost epitaxial to the surrounding Nb-bearing phase. These experiments showed that enhancing heterogeneous nucleation could be used as a tool for phase shape modification.
Fig. 5. (a) High resolution TEM study of the complex precipitate in a modified austenitic stainless steel: TEM image of boundary between Ti-bearing (dark) and Nb-bearing (white) phases with scanning line, (b) EDX line scan, and (c and d at higher magnification) electron diffraction from overlapped boundary between two phases.

2.2 Modification of primary $\beta$-AlFeSi dendrites in aluminum alloy by alloying and melt shearing

**Objective and approach.** Recycling of postconsumer aluminum scrap is the necessary technological cycle for reducing the energy consumption of aluminum production and for industry sustainability. In contrast to ferrous metals, specific thermochemical constraints limit the depth of melting purification of aluminum scrap from harmful alloying elements. Accumulation of impurities (mainly Fe) downgrades the quality of secondary aluminum alloys and can cascade forming non-recyclable scrap. The nature of harmful effects of accumulated impurities is related to the formation of a large and brittle primary $\beta$-FeSiAl intermetallic phase during solidification of secondary cast aluminum alloys (Fig. 6a). The refining of the primary solidified Fe-containing phase in secondary aluminum alloys can be achieved by restricting phase growth during casting solidification. The objective of this test was to verify a possibility of mitigation of brittle primary complex Fe-containing intermetallic phases formed during the solidification of secondary aluminum alloys by controlling growth using Mn-alloying and semi-solid melt shearing. This effective way to limit growth of prime $\alpha$-Al dendrite by enforcing melt convection in semi-solid temperature interval was discovered by Flemings [25, 26]. Such melt shearing processes were suggested to change shape of $\alpha$-Al prime dendrite to globule type which leads to improve the mechanical properties of aluminum alloys [27, 28].

![Fig. 6](image)

**Experimental results.** Briefly, plate shape $\beta$-AlFeSi phase in Al-7%Si alloy contaminated by 2% Fe (Fig. 6a) was transformed into compact significantly finer crystals (Fig. 6b) by combination of additional 1% Mn-alloying and melt shearing at the precipitation temperature range. In both cases, the melt was gravity poured into the simple shape no-bake molds. To design process, the experimental thermal curves was
obtained from the cast \textit{Mn}-modified hypoeutectic \textit{Al-Si} alloy contaminated by \textit{Fe} (Fig. 6c). The alloy showed the temperature of precipitation of \textit{AlFeMnSi}-intermetallic phase above the \textit{a-Al} dendrite liquidus temperature. After forced melt convection in temperature range between \textit{AlFeMnSi}-intermetallic phase precipitation and \textit{a-Al} dendrite liquidus, the alloy was poured into the identical no-bake sand molds with thermocouple. The selective refinement of the shape of \textit{Fe}-bearing phase has important advantages because will allow eliminate detrimental effect of plate type intermetallic phases on ductility of secondary aluminum alloy.

\subsection{2.3. Shape Modification of Covalent Crystals in Hypoeutectic \textit{Al}-alloys}

\textit{Hypothesis}. Cast aluminum and magnesium alloys reinforced by intermetallic phases are considered for high temperature and wear applications (engine pistons); however, undesirable angular shape of intermetallic phases limits it industrial usage. The published studies demonstrate that faceted angular shape phases with covalent atomic bonds (such as primary \textit{Si} and \textit{Mg2Si} phases in hypereutectic aluminum alloys) could be modified by \textit{Na} and \textit{P} additions. Both elements, \textit{Na} and \textit{P}, are well known donor type impurities in \textit{Si} covalent crystals and also change the shape of primary \textit{Si} crystals in hypereutectic \textit{Al-Si} alloys (Table 3). There are two types of donor impurities in covalent crystals: (i) the substitutional, which can substitute atoms in covalent crystals and create extra conduction electrons and (ii) interstitial, whose atoms have an easily removable electron and a small ionic radius. For example, atoms of \textit{P} having 5 electrons on its exterior shell (3s\textsuperscript{2}3p\textsuperscript{3}) can substitute atoms of \textit{Si} with 4 electrons on the exterior shell (3s\textsuperscript{2}3p\textsuperscript{2}) creating an extra conduction electron. Interstitial impurity \textit{Na} can inject an electron from it 3s\textsuperscript{1} exterior electron shell.

| Table 3. Electron structure of covalent phases and donor modifiers \cite{6}. |
|----------------|----------------|----------------|----------------|
| \textbf{Alloy} | \textbf{Phases} | \textbf{Electron} | \textbf{Modifiers} |
| \textit{Si}   | \textit{Si}    | 4              | \textit{P} \textit{Na} |
| \textit{Al-Sb} | \textit{AlSb} | 3-5            | \textit{S} \textit{Se} \textit{Te} |
| \textit{Al-Mg-Si} | \textit{Mg2Si} | 2-4            | \textit{Li} \textit{Na} |
| \textit{Mg-Si} | \textit{Mg2Si} | 2-4            | \textit{P} \textit{Na} |

The following hypothesis was suggested to describe a possible mechanism of the shape modification of phases with covalent atomic bonds by donor type additions. Donor type modifiers, captured by growing covalent crystals, will significantly increase the number of free electrons and change the type of phase transformation from “metallic melt → solid crystal with covalent atomic bonds” in an unmodified system to “metallic melt → alloyed by donor impurities crystal having free electrons”. This action of donor impurity could decrease the electron’s component of melting entropy (Table 1) and affect the shape of solidified phases, according to Jackson’s hypothesis \cite{2}.

\textit{Experimental}. A hypereutectic (18 wt. \%\textit{Si}) binary aluminum silicon alloy was melted under a protective argon atmosphere in a resistance furnace using pure aluminum (99.99\%) and silicon (99.999\%). The 50 g specimens were melted, modified by \textit{Na} or \textit{P} and cooled in crucibles of pure alumina. The cooling curves were recorded with \textit{K}-type thermocouples using the SCXI National Instruments data acquisition system. The single thermocouple thermal analysis technique (first derivative \textit{dT/dt} vs \textit{T}) was used to qualify the critical points of phase transformation. The changing bulk electrical conductivity of heterogeneous alloys
could be a result of altering phase’s properties as well phase shape modification. The 4-point method was used for measurement of a bulk alloy electrical conductivity. The Electron Beam Induced Current (EBIC) method was applied for in-situ measurement of electrically active sites in microstructure with a high SEM resolution [29]. Base and 0.05 wt.% Na modified specimens were mechanically polished and analyzed using the same angle, electron beam voltage (2kv), x350 magnification and other parameters with a JEOL JSM6100 SEM. Statistical evaluation of the gray scale level in different phases was obtained by OPTIMAS software in 10 fields on each specimen.

Results. The microstructures of a base and a modified hypereutectic (18% Si) binary Al-Si alloys are presented in Fig. 7. The unmodified alloy has coarse eutectic and primary octahedral and star-like faceted Si crystals with 200–250 μm the average size. In hypereutectic alloys, 0.05 wt.% Na additions refine the primary polyhedral angular silicon crystals into more compact, near spherical shapes, which were surrounded by a halo of the α-phase (Fig. 7b, c). The addition of 0.05 wt.% P increases the quantity of primary silicon crystals and decreases their average size by 3-4 times (Fig. 5d). In this case, the shape of the primary Si crystals was converted to compact with faceted planes; however, the coarse structure of the α-Al–Si eutectic does not change.

![Fig. 7. Microstructures of aluminum alloys with 18% Si: (a) base case, (b, c) modified by 0.05 wt.% Na, and (d) by 0.05 wt.% P.](image)

Thermal analysis showed (Fig. 8) that Na modification significantly decreases the formation temperature (liquidus) of primary Si while transformed angular primary Si-crystals into near spheroids (Fig. 7b, c). On the contrary, P modification increased a temperature of primary Si formation while size modification. It is interesting, that in both modified hypereutectic Al-Si alloys with Na and P additions, decreasing a time of solidification was observed in the specimens solidified at the same cooling conditions. This could be considered as an indicator of decreasing latent heat in alloys modified by donor type impurity.
Results of the statistical analysis of EBIC data in the alloys are shown in Fig. 9a. The average values of EBIC were significantly higher in \( \alpha-Al \), which has metallic conductivity, compared with primary \( Si \) crystals, which have covalent atomic bonds. Modification had no influence on the statistical distribution of the value of EBIC taken from \( \alpha-Al \). At the same time, the modified \( Si \) crystals had a higher value of absorbed electron current and their electronic properties fell between pure covalent \( Si \) crystals and metallic \( \alpha-Al \). The results of the measurements of bulk electrical resistivity of the alloys treated by different additions of \( Na \), indicated that \( Na \) additions decreased electrical resistivity of hypereutectic \( Al-18\% Si \) alloys (Fig. 9b). SEM/EDS analysis of hypereutectic \( Al-18 \) wt.% \( Si \) alloys modified by 0.05 wt.% \( Na \) showed the higher level of \( Na \) concentration in \( Si \) phase when compared to surrounding \( \alpha-Al \) (Fig. 10). This analysis indicated that \( Na \) was captured by growing \( Si \) crystals.
3. DISCUSSION

The different methods were experimentally tested in this article for shape control of primary solidified crystals in cast alloys. These methods triggered different mechanism of shape modification: changed precipitate nucleation, phase growth, interfacial phenomena, and also can employ different near field effects in close proximity from solidification front. The shape modification of the several primary intermetallic phases precipitated from the melt in industrial and modeled alloys was studied by using the specially selected additions and melt shearing. The experimental data obtained in this study were used for discussion of the possible mechanisms of shape modification of primary intermetallic and covalent phases in cast multicomponent alloys.

The first studied mechanism of shape modification is related to enhancing heterogeneous nucleation. Enhancing nucleation made dendritic and plate shape faceted phases more compact and smaller in size. This effect was observed in austenitic Cr-Ni-Nb steel treated by Ti (Fig. 4) and in hypereutectic Al-18 wt.% Si alloy treated by P (Fig. 7d). In the first case, heterogeneous nucleation sites were detected and electron diffraction showed that Ti-bearing seed was almost epitaxial to Nb-bearing phase. The heterogeneous nuclei had similar crystallographic parameters to nucleated phase and these phases precipitated almost epitaxial (Fig. 5). Existence of AlP particles inside the primary Si phase in hypereutectic Al-Si alloys was experimentally proven in previous study [10]. Enhancing heterogeneous nucleation of Si phases by P addition was supported by thermal analysis. Thermal analysis of P-treated hypereutectic Al-Si alloy showed decreasing undercooling necessary for precipitation of heterogeneously nucleated primary Si phase (Fig. 8).

The shape of solidified phases is controlled by growth mechanisms and a nucleation event could provide an indirect effect on crystal shape, which was observed in modified austenitic steel (Fig. 4b) and Al-Si alloy (Fig. 6d). The small crystals have near equilibrium shape as predicted by Gibbs-Curie-Wulff’s theorem and surface topology as followed from Jackson’s or Cahn’s models. The further morphological evolution of the shape is a result of instabilities in front of freely growing crystal. In the studied cases, enhancing heterogeneous nucleation changed the macro-shape of crystals without transformation of their faceted interfaces (Fig. 4b and Fig. 7d). It could be stated that, enhancing heterogeneous nucleation prevents development of shape instability by reducing crystal sizes.

The phase shape modification by melt shearing in mushy zone involves several possible effects. Melt shearing could brakes large plate-like primary β-phase in Fe-bearing aluminum alloys activating self-nucleation. This mechanism provides similar to effect on the phase shape as described above enhancing heterogeneous nucleation. However, changing near-field temperature and concentration promote forming compacted intermetallic phases with smooth interface (Fig. 6b).

The mechanism of shape modification covalent crystals by donor type impurities is based on changing the electronic structure of solidified phase (Fig. 2). SEM/EDS analysis of hypereutectic Al-18 wt.% Si alloys
modified by 0.05% Na showed the higher level of Na in a Si phase when compared to surrounding α-Al (Fig. 10). The donor impurities will significantly change the electronic properties of the growing phases by injecting a significant number of "free" conduction electrons into a covalent crystal. The measurement confirmed that Na modification increased the bulk electrical conductivity of the hypereutectic Al-Si alloy (Fig. 9b). An effect of increasing electrical conductivity by the Sr-additions into a modified Al-Si alloy was also found [30]. This could be due to a change in the electrical resistivity of individual phases or to the effect of phase morphology. The EBEC measurement partially clarified these effects and showed that Na modification increases an absorbed electron current and conductivity of a Si phase (Fig. 9a). A donor type impurity has the possibility to inject a huge amount of conduction "free" electrons into covalent crystals. For example, a pure semiconductor contains $10^{12}$-$10^{13}$ "free" electrons per 1 cm$^3$, while a metal has $10^{22}$ "free" electrons per 1 cm$^3$ and only a ppm level of a donor addition can donate up to $10^7$ "free" extra electrons per 1 cm$^3$. This action could dramatically change the conduction properties of a covalent crystal. A high solidification temperature significantly increases the number of "free" electrons in covalent crystals by decreasing the energy gap between valence and conduction bands.

Doping donor impurity could partially eliminate the electronic component of melting entropy in covalent crystals (Table 1). Pure covalent Si has significantly higher latent heat (1650 J/g) when compared to Al with metallic properties (390 J/g). Published data, obtained with using DSC method, showed an increase of latent heat from 425-435 J/g in hypereutectic to 470-490 J/g in near eutectics Al-Si alloys [31]. In our experiments, Na modification decreases the solidification time of primary Si phases and Al-Si eutectic which could indicate about decreasing latent heat release. The effect of P additives on solidification time of primary Si phase was significantly less when compared to Na additives while there were no changes in thermal analysis of Al-Si eutectic with P additions. The special studies needed to be performed to prove this effect. The fact of the change in latent heat of different alloys after modification was also described elsewhere [32-34]. Hu and Pan [32] described a lower value of latent heat in modified by P and Ti hypereutectic aluminum silicon alloys. Benawy and Fredriksson [33, 34] found lower values of latent heat in modified and rapidly cooled Al-Si alloys; more experiments needed to be perform to clarify this possible effect.

Accordingly Jackson theory, the changing in melting entropy could promote growth of a smoother diffuse interface instead of angular faceted crystals in unmodified alloys. When the hypereutectic Al-Si alloy was modified with Na the shape of some primary Si crystals transformed to near spherical with a smoother surface (Fig. 7c) while, when modified with P, Si crystals remained faceted with a significantly smaller size (Fig. 7d). Interstitial donor impurities, such as Na, could provide a stronger effect on the change of electron states in primary covalent Si crystals when compared to a substitutional impurity, such as P.

The suggested hypothesis of shape modification of phases with covalent atomic bonds by donor type impurities also enables prediction of the modifier composition for the other alloys. For example, the modifiers for the phases with covalent atomic bonds, such as AlSb, could be predicted based on information about the electronic structure of elements and phases (Fig. 11). The AlSb phase is formed by the elements from the 3rd (Al) and the 5th (Sb) groups and substitutional type of donor impurity will be one of the elements from the 6th group (S, Se, or Te) having an extra electron on an exterior p-orbital.
The experimental microstructures, which are given in Fig. 12, confirm that Te modifies the shape of crystal AlSb in a hypereutectic Al-Sb alloys. Also, the specific zones at the center of Te-modified compact AlSb crystals can be observed in a Al-5.5 wt.% Sb alloy under higher magnification (Fig. 12c). EDS of the Te modified compact AlSb crystals shows that their center contains a high concentration of Te (63 at. % Al, 13.8 at. % Sb, and 23 at. % Te). In this case, the two discussed mechanisms (enhancing heterogeneous nucleation by an aluminum telluride intermetallic phase and changing electronic structure of covalent AlSb crystal by Te-donor type impurity) could be responsible for shape modification.

There are other mechanisms which were not discussed in article could be considered. Modifier can change the growth conditions by reacting with the surface active impurities in the melt. This mechanism could be important of graphite spheroidization in cast iron treated by Mg. The adding or removing the surface active elements from the melt can effect on the shape of precipitated phase by changing the interfacial energy anisotropy and developing or removing the impurity interface barrier. In addition, the different types of atomic imperfections on ideal atomically flat surface of faceted crystal, such as dislocations and vacancies, exist because they allow increasing crystal growth velocity. The modifier atoms and impurities in the melt can have preferred positions on growing faceted interface and interact with dislocations and vacancies. The possible effects of these interactions on the shape modification of graphite in cast iron and Ni-C alloys were hypothetically discussed [35, 36]. Finally, it is interesting to note, that several decades ago Tiller and Takahashi [37] showed that the solid-liquid interface energy has an electron component which is determined by the difference of electron energy in the crystal and the melt. The donor impurities in covalent crystals can change the interfacial energy of crystals which will affect its shape.

CONCLUSIONS

Several hypothesis about the mechanism of modification of the primary faceted crystals in cast aluminum and iron based alloys were experimentally tested and discussed: (i) by enhancing heterogeneous nucleation, (ii) by enforcing melt convection in semi-solid temperature interval, and (iii) by changing electronic
properties of the solidified phases with covalent atomic bonds by donor type impurities. It was shown that, the enhancing heterogeneous nucleation changes the crystal’s shape to a more compact and smaller size, while the crystals still having a faceted interface. Enforcing melt convection and changing electronic properties of covalent crystals by donor type impurities were both effective in modification of the interface topology and therefore in crystal shape but different mechanisms were responsible for this effect. Considering these mechanisms, it is possible to make first selection of the shape modification processes while more studies needed to be done in future.

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