Function of AlN in the Formation of Grained Structure of Microalloyed Steel

D. Kalisz*, S. Gerasin
AGH University of Science and Technology, Faculty of Foundry Engineering
ul. Reymonta 23, 30-059 Kraków, Poland
*Address: e-mail: dak@agh.edu.pl

Submitted on 20.11.2015; accepted for print on 29.12.2015

Abstract

Obtaining high resistance parameters is a result of generation process of fine-dispersive phases of nitrides, carbides and carbonitrides in the process of solidification and thermal processing. The precipitates formed as a consequence of introduction of Ti, V, Nb and Al play the role of grain growth inhibitors. Aluminum forms a separate AlN phase, which does not form a solution with the remaining nitrides and carbonitrides. This paper is devoted to the process of AlN inclusions formation in the process of solidification of steel with a microaddition of Al. The process was simulated with the use of own computer program. The calculations were performed for the cooling conditions 100 and 500K/min. The obtained results were illustrated with figures. The influence of the casting rates on the process of aluminum nitride formation as pure non-metallic phase or component of the oxidic solution was analyzed. It was observed that the formation of AlN precipitates takes place easier when nitride is part of a solution composed of a non-metallic phase and at a higher cooling rate. This means that the higher cooling rate, and consequently higher casting rate, favor the precipitation processes and so the fine-grained structure. The results obtained for AlN prove that precipitates formation is conditioned by the concentration of both components. The quantity of the obtained compound will depend on the content of more deficient element, in this case nitrogen. The final distribution and size of particles of second phase will depend on the diffusion process of AlN particles' growth.

Key words: AlN precipitates, segregation, computer simulation, calculation, microalloyed steel

1. Introduction

Steels with microadditives are applied in machine industry, ship industry, mining, liquid gas transport, pressure tanks and other construction materials. The high metallurgical purity, fine-grain structure and high level of plasticity at optimum ductility and high resistance to breaking are the most important properties of these materials. The increasing requirements for these materials caused that Advanced High Strength Steel (AHSS) materials were worked out; the strength of the material was increased by the fine-dispersive particles and Thermomechanical Controlled Processed (TMCP), i.e. controlled plastic deformation and thermal processing [1]. High strength properties of microalloyed steels can be obtained by comminuting grains and precipitation reinforcement. Such non-metallic particles precipitates as: nitrides, carbides and complex carbonitrides play an important role in the formation of the structure. The condition of obtaining a fine grained ferritic structure is generation of a given amount of fine-dispersive precipitates which originally hinder the growth of austenite grains, and after the transformation of austenite - ferrite; as a consequence a fine ferritic structure is obtained [2]. Ferrite can be produced if granulation centers exist inside austenite. Titan, niobium and vanadium form carbides and carbonitrides, which in the course of heating below 1250 °C are not dissolved completely, therefore become nuclei of newly formed grains while cooling, thanks to which the steel has a fine-grain structure. A minimum addition of these elements to steel contributes in its fine-grained structure. In the solidification process they form...
dendritic carbonates and carbonitrides distributed on the grain boundary. This results in lower brittleness of the binder. While introducing microadditives, especially Nb and Ti the sulphur content should be reduced in steel. Sulphur with Ti, Nb and C forms dendritic carbosulfides which increase the liability to cracking at high temperatures. Apart from microadditives, e.g.: Nb, V, Ti this function is also played by Al [3]. The presence of aluminum in liquid steel is a result of introduction of this element in the deoxidation process in the ladle, which precedes the casting process.

Aluminum has a high chemical affinity with oxygen and nitrogen; they form nitride AlN of a hexagonal network. Other nitrides and carbides have a wall-centered network, therefore may dilute one another, with carbonitrides as a result. This does not refer to AlN, which does not form a solution with other nitrides and forms a separate phase of nitride or is a component of oxidic solutions [4]. As far as solubility in austenite is concerned, nitride AlN shows higher solubility by TiN and comparable with that of NbN and VN (fig. 1).

Fig. 1. Solubility of nitrides and carbides in austenite

Therefore, more TiN is more efficient for the grain size control in higher temperatures. The nitrogen content in steel influences the effect of comminution.

2. Numerical modeling of microsegregation and AlN precipitation in the process of steel solidification

Simulation calculations were performed with the use of own computer program basing on a Matsumiya concept, the assumptions of which have been presented in works [5]. The numerical method is based on the Fick's diffusion equation and is very useful for the analysis of the process of inclusions formation in steel, mainly oxides and sulfides and also nitrides and carbides. On this basis the amounts of components precipitated in a given moment of time can be calculated, and so in a given location with respect to the dendritic axis. This also allows for correcting the composition of liquid after each time step, in which the precipitation occurred, and consequently for determining the correct temperature of crystallization-end.

Modeling with the use of the finite difference method is based on the diffusion equation used for each of the components [9-22]:

$$\frac{\partial C}{\partial t} = -D \cdot \frac{\partial^2 C}{\partial x^2}$$  \hspace{1cm} (1)

It is transformed to the general:

$$\frac{C_i - C_i^{\infty}}{\Delta t} = D \cdot \left( \frac{C_i^{\infty} - C_i^{\infty-\Delta t}}{\Delta x} - \frac{C_i^{\infty} - C_i^{\infty+\Delta t}}{\Delta x} \right)$$ \hspace{1cm} (2)

and applied for the calculation domain divided into, e.g. 200 cells (i denotes the successive number of the cells). For a cell m, w in which the solidification takes place at a given moment, the following equation is applied:

$$C_m^t = k \cdot C_L^t$$ \hspace{1cm} (3)

Using the equation of the component balance and introducing the back diffusion parameter α we obtain the course of solidification of each component in liquid phase in a function of advancement of the process, measured with the participation of the solid phase. The calculation of precipitates requires comparing of the boundary value of the product of solubility and the real value and the correction of concentrations of components making up the precipitate (at each step) [7-9, 12-15, 20-22].

Calculations were made for microalloyed steel and the chemical composition was established on the basis of chemical analysis of samples from the ingot (table 1).

Table 1 – Chemical composition of steel assumed for calculations / %.

<table>
<thead>
<tr>
<th>Steel</th>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>P</th>
<th>S</th>
<th>V</th>
<th>Al</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.21</td>
<td>1.0</td>
<td>0.25</td>
<td>0.018</td>
<td>0.005</td>
<td>0.008</td>
<td>0.024</td>
<td>0.009</td>
</tr>
</tbody>
</table>

3. Results of calculations

The changing content of aluminum and nitrogen during solidification of a steel ingot has been presented in figures 2 to 5 (table 1) with a microaddition of Al at a cooling rate 100 K/min and 500 K/min, on the assumption that the activity of the precipitated aluminum nitride equals to $a_{\text{AlN}} = 1$, $a_{\text{AlN}} = 0.6$, $a_{\text{AlN}} = 0.2$, respectively.
The form of the nitride, i.e. whether it occurs as a component of a non-metallic phase or a pure substance has a decisive influence on the possibility of its generation. Presently applied thermodynamic databases of this effect are incomplete and this mainly can be attributed to the lack of experimental data, therefore the commercial programs have a problem with defining...
this issue; in this case assumptions were made about the activity of the AlN phase.

The boundary value of the solubility product is calculated in a simplified form on the basis of a constant equilibrium of precipitate (AIN) formation. If a few compounds are precipitated simultaneously, then the aluminum nitride will be a component of the solution and its activity will be lower than 1. Consequently, the boundary value of the solubility product will also be lower than unity and the precipitate will be formed earlier (fig. 6). The course of the equilibrium and real solubility product reveals that the AlN precipitates are formed more easily at a higher cooling rate, which signifies that the increased casting rate favors the process of fine-grain structure production (fig. 6-7). The results obtained for AlN prove that the concentration of both these components decide about the precipitates formation. The amount of the produced compound will depend on the content of the more deficient element, in this case nitrogen (figs. 4 to 5).

4. Diffusive increase of AlN phase

The simulation of the diffusive process for a single spherical particle of radius r, which is disposed in the center of the spherical zone of radius L, is based on the following dependences:

- thermodynamic condition of aluminum nitride formation from components dissolved in liquid steel,
- equation for the diffusive stream of mass transport (1st Fick’s Law) for aluminum and nitrogen,
- equation of mass balance.

Radius L of an area results from the number of particles of non-metallic precipitates. The following reaction of nitride formation takes place on the surface of the particle [9]:

\[ [\text{Al}] + [\text{N}] = \text{(AlN)} \]  

(4)

The equilibrium constant in this reaction:

\[ K = \frac{a_{\text{AlN}}}{a_{\text{Al}} \cdot a_{\text{N}}} \]  

(5)

where:

- \( a_{\text{AlN}} \) – activity of aluminum nitride,
- \( a_{\text{Al}} \) – activity of aluminum,
- \( a_{\text{N}} \) – activity of nitrogen,
- \( f_{\text{Ni}} \) – coefficient of activity after Henry,
- \( C_{\text{Al}} \), \( C_{\text{N}} \) – equilibrium concentration Al and N.

On the assumption that the activity of components is constant within the low range of concentration of both elements, we have a straight value of the products of \( C_{\text{Al}} \) and \( C_{\text{N}} \) for a given temperature. For calculating values of both multiplication factors we need an assumption about the equality of diffusive streams for both reagents on the surface, where the compound is formed (i.e. surface of the precipitate) [9]:

\[ y_{\text{Al}} = y_{\text{N}} \]  

(6)

Hence

\[ D_{\text{Al}} \frac{C_{\text{Al}} - C_{\text{Al}}^e}{M_{\text{Al}}} = D_{\text{N}} \frac{C_{\text{N}} - C_{\text{N}}^e}{M_{\text{N}}} \]  

(7)

From dependence (7) we have concentrations of both components on the surface of the growing precipitate. The precipitate growth rate for the AlN compound gives equation:

\[ \frac{dr}{dt} = \frac{M}{100 \cdot s \cdot M_i} \rho_{\text{m}} \rho_1 D_{\text{AlN}} \left( C_i(t) - C_i^e \right) \]  

(8)

where:

- \( M_i \) – atomic mass of metallic component,
- \( x \) – stoechiometric component of metal in the compound,
- \( M \) – molecular weight of a compound forming the precipitate,
- \( \rho_{\text{m}} \) – density of steel kg/m³,
- \( \rho_1 \) – density of precipitate kg/m³,
- \( D_{\text{AlN}} \) – diffusion coefficient of component „i“ m/s,
- \( C_i(t) \) – average concentration of component „i“ in a given moment of time.
- \( C_i^e \) – concentration „i“ stemming from the equilibrium of compound formation reaction. Concentrations are expressed in weight percent.

In the course of diffusive growth of a particle the average concentration of component „i“ decreases in the analyzed area, i.e. zone of radius \( L \), where the given particle is disposed. This value results from the mass balance. If we assume a uniform initial radius of a particle \( r_0 \) and initial concentration of component \( C_i(0) \) we obtain the following dependence:

\[ \frac{4}{3} \pi L^3 \rho_{\text{m}} \frac{C_i(0)}{100} = \frac{4}{3} \pi r_0^3 \rho_1 C_i(0) + \frac{4}{3} \pi \left( L^3 - r_0^3 \right) \]  

(9)

5. Conclusions

The results obtained in this paper may be used for evaluating the selection of parameters of continuous steel casting, i.e. casting rate, cooling conditions, selection of chemical composition of a given type of steel. The microsegregation model taking into account the precipitation processes provided information about the distribution of particles in the cast ingot. No information is obtained about the size of these precipitates nor about their size distribution. The diffusion of the least numerous component in the solution may decide about the particles formation in the second phase. In real conditions the precipitation processes co-operate, which means that the precipitation of oxides affects the formation of nitrides and inversely. Another important factor affecting the AlN phase formation is the presence of components which bind nitrogen, e.g. Ti and the end content of oxygen dissolved in steel. Taking into account the back diffusion effect in the calculations means that the transport of metallic liquid phase takes place not only from the solid to liquid phase, but also partly to the solid phase. As a consequence, taking into account the back diffusion
effect has an influence on segregation, and resulting in weakening of this effect and activation of the precipitation processes.

Acknowledgements

This study was solved within the framework of the project Reg. No. 11.170.318 task 14 at financial support of Ministry of Science and Higher Education Republic of Poland.

References

Streszczenie

Uzyskanie wysokich właściwości wytrzymałościowych jest wynikiem procesów wydzielenia drobno dyspersyjnych faz azotków, węglików i węglikoazotków w procesie krzepnięcia i obróbki cieplnej. Rolę inhibitora rozrostu ziaren pełnią wydzielenia powstałe w wyniku wprowadzenia: Ti, V, Nb oraz Al. Aluminium tworzy odrębną fazę AlN, która nie tworzy roztworu z pozostałymi azotkami i węglikoazotkami. Obecna praca zajmuje się zjawiskiem powstawania wydzielen AlN w procesie krzepnięcia stali z mikrododatkiem Al. Symulacją procesu wykonano przy pomocy własnego programu komputerowego. Obliczenia przeprowadzono dla warunków chłodzenia 100 i 500K/min. Otrzymane wyniki zilustrowano w formie wykresów. Badano wpływ szybkości odlewania na proces wydzielenia azotku glinu jako czystej fazy niemetalicznej lub składnika roztworu fazy tlenkowej. Stwierdzono, że tworzenie wydzielen AlN, zachodzi łatwiej wówczas, gdy azotek jest składnikiem roztworu złożonego z fazy niemetalicznej oraz przy większej szybkości chłodzenia. Oznacza to, że zwiększenie szybkości chłodzenia, a w konsekwencji zwiększenie szybkości odlewania sprzyja procesowi wydzieleniowemu, a w rezultacie powstawaniu struktury drobnoziarnistej. Wyniki uzyskane dla AlN są potwierdzeniem, że o możliwości powstawania wydzielenia decydują stężenia obydwu składników. Ilość powstalenego związku będzie zależeć od zawartości pierwiastka bardziej deficytowego, w tym przypadku jest nim azot. O ostatecznym rozkładzie i wielkości cząstek drugiej fazy będzie decydować proces dyfuzyjnego wzrostu cząstek AlN.