Effect of titanium additions to low carbon, low manganese steels on sulphide precipitation

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CHAPTER SIX

Initial experiments on segregation study

6-1 Introduction

It has become increasingly obvious that inclusions can be utilized as an effective tool for the control of microstructure [9]. Manganese sulphide precipitates are known to crystallize and precipitate preferentially in interdendritic regions during solidification, due to the segregation of manganese and sulphur and these inclusions have traditionally been used for the dual purpose of improving the machinability and controlling of grain structure in steel [24].

Emi and co-workers combined Laser Scanning Confocal Microscopy (LSCM) with infrared heating in the 1990s [85]. Shibata et al. [21] proposed a new approach to the study of solidification by using this instrument and Yuki et al. [76] were able to observe in-situ and at high temperature, the dynamic growth of MnS crystals in an Fe-C alloy [76]. Their work followed various attempts in the past [22-24] to observe MnS formation on the surface of steels during microsegregation. On the other hand, macrosegregation, which occurs over large distances due to the physical movement of liquid or solid phases has not received the same attention in the literature [25]. In the current study, a newly developed concentric solidification technique is employed to observe in-situ the events occurring during
solidification and an attempt is made to observe the precipitation through long distance segregation in a low carbon, low manganese and titanium added steel.

6-2 Experimental method

The bulk chemical composition of the steel slab that was studied is shown in Table (6-1). Previous studies [11] concerned with inclusions in low carbon, low manganese steels have indicated the presence of oxide inclusions, mostly alumina, and MnS stringers and we have chosen the composition shown in the table to enable us to examine the effect of titanium on the morphology, composition and occurrence of sulphide precipitates.

<table>
<thead>
<tr>
<th>Element</th>
<th>C</th>
<th>Mn</th>
<th>S</th>
<th>Al</th>
<th>Ti</th>
<th>Si</th>
<th>N</th>
<th>P</th>
<th>Ni</th>
<th>Cr</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Percent</td>
<td>0.095</td>
<td>0.29</td>
<td>0.009</td>
<td>0.03</td>
<td>0.024</td>
<td>0.005</td>
<td>0.0037</td>
<td>0.018</td>
<td>0.024</td>
<td>0.022</td>
<td>0.026</td>
</tr>
</tbody>
</table>

Specimens were selected from the edge of slab as shown in Figure (6-1). The positions of specimens assure that the samples are not affected by the macrosegregation of elements at the centre of slab and matched with the reported chemical composition in Table (6-1). A Concentric Solidification Technique [26] has been employed to observe the segregation during solidification. The process is explained in detail in Chapter (3-7-1). This procedure ensures that a stable melt pool is formed with a solid rim surrounding the liquid pool. This arrangement simulate the microstructural development in horizontal slice of a slab as it moves down the mould in a vertical continuously cast slab as shown in Figure (6-2). Macrosegregation of elements occurs as the section moves down the mould in similar fashion to the movement of growing solid phase towards the centre of specimen in the concentric solidification technique. Liquid movement, due to gravitational forces and convention currents in the liquid contributing to macrosegregation are clearly not considered. The cooling rate of 20°C/min selected for this experiment is similar to the cooling rate at the centreline of a continuously cast slab.
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Figure (6-1): Schematic illustration of samples positions in slab prepared for concentric solidification technique

Figure (6-2): Schematic illustration of solidification in continuously cast slab and concentrically solidified specimen
4-3 Results and discussion

During heating, some small particles floated on the surface of the liquid as shown in Figure (6-3). These particles were most probably original inclusions that floated out or were the result of reaction between liquid steel and the crucible or furnace atmosphere but they disappeared after a few minutes, driven by Marangoni forces out of the field of view towards the solid rim.

![Figure (6-3): Floated particles on the surface of liquid steel during heating in LSCM](image)

During cooling, solidification of $\delta$-ferrite proceeds from the solid rim towards the centre of the disc-shaped sample as shown in Figure (6-4-a). The growth of $\delta$-ferrite from the liquid at the solid rim in a concentric solidification experiment is depicted in Figure (6-4-a to c). Figure (6-4-d) shows the situation 1 s later: upon cooling below the peritectic temperature, a thin layer of austenite progresses along the liquid–solid interface. Following the peritectic reaction, austenite grows into the liquid by an advancing planar interface, and the pre-existing $\delta$-ferrite also transforms to austenite.
On occasion, some dendrites formed ahead of the advancing liquid/solid interface within the molten pool as shown in Figure (6-5). This phenomenon was observed very rarely on simple Fe-C steels so it can be concluded that non-metallic inclusions and/or precipitates formed in the liquid pool can act as nuclei for new ferrite grains.
Following solidification, the remaining liquid, enriched in alloying elements, finally solidified in the centre of the disc. Although impossible to observe, the remaining liquid was specifically enriched in carbon and the final liquid that solidified contained a carbon concentration significantly higher than the bulk specimen. This is what happens during continuous casting of steel.

In the final stages of solidification, a group of small particles suddenly appeared on the surface of the sample and grows very quickly to cover most of the surface of the remaining liquid as shown in Figure (6-6). Figure (6-7) illustrates the solidification that results to segregation and precipitation in concentrically solidified specimen schematically. Precipitates form between dendrites from the last liquid squeezed between grains.

Following the observation of the formation of these particles in the confocal microscope, the sample was transferred for observation in a scanning-electron microscope. Figure (6-8) shows a typical SEM micrograph of the precipitates that formed during solidification in the segregated area. EDS analysis of similar precipitates indicates the presence of titanium and sulphur within the particles while the manganese content is very low as shown in Figure (6-9). It is not possible to determine quantitatively the carbon distribution using EDS analysis and hence, it is not possible to distinguish between TiS and Ti₄C₂S₂. An attempt to make this distinction was the subject of further studies by employing Transmission Electron Microscopy (TEM).

Figure (6-6): In-situ observation of sulphide precipitation on the surface of the LSCM sample
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Figure (6-7): Schematic illustration of solidification and precipitation by concentric solidification technique

Figure (6-8): SEM photograph of a colony of precipitates
The rod-like morphology of the precipitates would suggest that they may have formed by an eutectic reaction but the LSCM observations did not provide any evidence of the occurrence of such a reaction. If it is the case, titanium sulphide particles (TiS) will form from the segregated liquid following cooling from the liquid state by the transformation of $L_1 \rightarrow L_2 + Fe(s) + TiS(s)$. Should it be assumed that this transition occurred, it is possible that the precipitates nucleate heterogeneously on the solid rim at the progressing solid/liquid interface. Although solid iron that may form through such a transformation cannot be distinguished in the SEM, the sudden appearance of a bright phase was observed on the
surface of the sample in the confocal microscope, associated with titanium sulphide particles as shown in Figure (6-10). This bright phase might well be solid iron.

![Image of solid steel and sulfides](image)

**Figure (6-10): Presence of liquid steel as well as two different solid phases (LSCM sample)**

Solid titanium sulphide will form by reaction (6-1):

\[
[Ti] + [S] \rightarrow \text{TiS(s)} \quad (6-1)
\]

The solubility product of this reaction, reported in literature [18] is:

\[
\log[\text{Ti}][\text{S}] = -13975/T + 5.43 \quad (6-2)
\]

Hence, the likelihood of titanium sulphide precipitation can be calculated as a function of temperature as shown in Figure (6-11). The horizontal line in this figure is the solubility product \([\text{Ti}][\text{S}]\) based on the bulk composition of the steel shown in Table (6-1). Consequently, precipitation of TiS is not possible in liquid steel until significant segregation of titanium and sulphur has occurred during solidification.

In order to confirm the chemical composition of particles and distinguish between titanium sulphide and titanium carbo-sulphides, samples were cross sectioned by a focused ion beam milling technique as shown in Figure (6-12). (This technique was described in more detail
in Chapter (3-4-1-3)). The figure illustrates that the top layer actually consists of two separate layers and the first layer does not merely consist of sulphides as may be concluded from the EDS analysis in the SEM.

Figure (6-11): Solubility product \([\text{Ti}]\text{[S]}\) for \((\text{TiS})_s\) precipitation as a function of temperature

Figure (6-12): Cross section of particles observed on the surface of concentrically solidified specimen in the LSCM, (a) to (d) illustrate the cross section at different magnifications
An attempt to fully characterise the nature of these layers, a TEM sample was prepared from these layers to investigate the nature of the particles as illustrated in Figure (6-13).

A bright field TEM image of the sample is shown in Figure (6-14). EDS analyses done on the two layers show the presence of titanium and oxygen in top layer and iron and sulphur in the layer underneath.
An X-ray map prepared from an area of the sample illustrated in Figure (6-15), shows that a porous layer of titanium oxide formed on top and the layer underneath consists of iron sulphide. The appearance of the layer indicates that titanium sulphide was formed in the solid state (as observed in the LSCM) and liquid iron sulphide formed between the liquid steel and the solid oxide. Since these two layers formed together on the surface, the EDX analyses in the SEM showed the presence of titanium and sulphur but it was not possible to detect oxygen due to the surface roughness of the sample. There is a possibility that titanium oxide nucleated on the surface followed by the nucleation of liquid iron sulphide on this oxide as there is evidence in the literature that sulphides can nucleate on oxide surfaces in liquid steel [10, 41, 46].
Further investigation indicated the formation of manganese sulphide in close proximity to the iron sulphide as illustrated in Figure (6-16). It seems that liquid iron sulphide and liquid manganese sulphide formed in close proximity to the solid titanium oxide.
In order to compare the composition and morphology of particles on the surface and at the cross section of the sample, the specimen was sectioned, approximately through the centre and the precipitates were further explored by using optical and scanning electron microscopy in the as-polished condition. These investigations will be discussed in Chapter 7.

Titanium oxide and iron sulphide formed on the surface, evidently because the oxygen partial pressure in the furnace chamber was not low enough to prevent the formation of titanium oxide. Although high purity Argon was used as the chamber atmosphere, the high affinity of titanium for oxygen and the possibility that a small quantity of air may have leaked into the furnace, caused the formation of titanium oxide on the surface of specimen.