On the Distribution of Inclusions formed during the Diffusion of Aluminum into Solid Iron at High Temperature

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The present work was aimed at obtaining knowledge about the formation of inclusions after solidification. A hole was bored in the solid iron containing oxygen and filled with a pure aluminum wire; and they were held at 1450°C for half an hour to three hours, in order to investigate the distribution of the formed inclusions. The results were obtained with the naked eye and by the microscope and the microanalyzer. The results are;

1. The stratiform inclusion group was formed near the boundary between liquid aluminum and solid iron, namely at the solid-liquid interface.
2. The inclusions were much smaller than those formed during the deoxidation of liquid iron with aluminum.
3. The stratiform inclusion group consisted singly or in various combinations, of alumina, spinel hercynite and wüstit.
4. The distribution of the inclusions forming the stratiform group could be successfully explained by assuming that the behavior was the same for the solubility of oxygen in solids as in liquids.

I. Introduction

We have conducted experiments by dropping aluminium wires onto liquid iron containing oxygen, with the thermal convection being negligible, to learn about the generation and growth mechanism of alumina inclusions formed during the deoxidation of liquid iron with aluminum(1)–(4). In that case, we paid particular attention to the inclusions group formed in a layer, and investigated the composition of the inclusions comprising the stratiform inclusions group, and summarized the formation and growth of the inclusions from the viewpoint of the effects of the initial oxygen content in the liquid iron and the reaction time of deoxidation. However, the formation and growth of inclusions during and after solidification, especially alumina inclusions, remain to be further investigated. This problem is very important, because the melt must be solidified and cooled both in industrial steelmaking and most laboratory experiments, and the decreased solubility of oxides in liquid or solid steel with decreasing temperature is one of the principal mechanisms by which the inclusions are formed. Thus, in an attempt to solve this problem, aluminum was diffused at a high temperature into solid iron containing oxygen.

II. Experimental Apparatus

Fig. 1 is a schematic cross section of the 15 kW vacuum Tammann furnace used for this experiment. This furnace, equipped with a 48Φ × 40Φ × 300 mm Tammann tube heater, in which a crucible support can be moved vertically, with a routine heating capacity of 1600°C, 1800°C in maximum. Prior to experiment, the distribution of temperature in the

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furnace was measured and the length of the uniform temperature zone (1450°C ± 5°C in our experiment) was found to be about 50 mm. This vacuum furnace was used under a mild atmosphere of argon gas. The used argon gas purifier was described in detail in the previous report (1).

III. Experimental Procedure

About 90 g of electrolytic iron and a suitable amount of iron oxide powder were put into a 26φ × 22φ × 60 mm flat-bottomed semi-fused alumina crucible. Then the furnace was fired and melting was carried out while flowing argon gas on the specimen. The melt was held at about 1600°C for an hour in order to uniformly dissolve the oxygen. Then, the furnace current was switched off and the crucible support was lowered until the crucible was out of the heater, and allowed the liquid iron to solidify very rapidly.

Using an electric drill, a 5φ × about 30 mm hole was bored down vertically in the cylindrical solid iron, containing oxygen, at a point 5 mm apart from the central axis of the cylinder. The hole was bored at the point apart from the center of the cylinder, because, though the specimens were cooled as rapidly as possible, we tried to minimize errors in the results due to the combination of the experimental results and the segregation of oxygen. Next the hole was degreased and cleaned with alcohol and ether, and then a pure aluminum wire (JIS 1st grade) was filled into the hole.

This specimen was again put into the crucible used for preliminary melting, and the crucible was set on the support in the Tammann furnace. Then, the crucible support was lowered until the crucible was out of the heater; the atmosphere in the furnace was replaced with refined argon gas, and the furnace current was switched on. After the thermocouple inserted in the middle part of the heater showed a furnace temperature of about 1450°C, the crucible support was raised rapidly, and the specimen was set in the uniform temperature part of the furnace. The temperature of the specimen was measured by means of the thermocouple, a hot-junction touching the surface of the solid iron. It took about ten minutes after setting the specimen in the heater before the temperature of the specimen reached 1450°C. The specimen was held at that temperature, and the oxygen dissolved in the solid iron and the aluminum diffused into it were allowed to react for a given time and then the furnace current was switched off and the crucible support was lowered to cool the specimen very rapidly.

The specimen was cut into two species along the surface containing the central axes of the specimen and the hole, and was polished. First, the specimen was observed with the naked eye and the microscope. Then, a 15φ × 10φ × 6 mm block containing the reaction interface was cut out of the specimen for electron probe X-ray microanalysis, and the matrix and the inclusions in the block were analyzed. A 100μ/min line scanning speed analysis and a point analysis were used for the quantitative analysis of the matrix, and a 10μ/min line scanning speed analysis and a point analysis were applied for the determination of the inclusions.

IV. Experimental Results

The melting of specimens was carried out keeping the initial oxygen content in the solid iron at about 0.05%, and with reaction times of about 1/2, 1, 2, and 3 hours. First, the specimen obtained was polished and observed with the naked eye. The results are shown in Photos. 1(a) and (b) which were photographed by means of a 25 mm and a 100 mm extension tubes, respectively. According to this macroscopic observation, it is seen that the inclusions formed distinguishable layers near the interface between liquid aluminum and solid iron.

Next, this specimen was observed by the microscope and the results are shown in Photo. 2. Here the aluminum-rich part is on the left side and the iron-rich part is on the right side. According to Photo. 2, it is seen that these inclusions were much smaller than those formed during the deoxidation of liquid iron with aluminum. Also, the inclusions formed two distinguishable layers near the interface between the liquid aluminum and the solid iron, as noticed by the macroscopic observation, Photo. 1.
(II), where few inclusions were formed. Photo. 2 (c) shows a part of group (II) which is in the iron-rich side. From this photograph, it is seen that the inclusions in group (II) were smaller than those in group (I). From the distribution of the inclusions, it is also recognized that the inclusions grow better with decreasing aluminum content in the matrix, but there is a maximum growth at a certain aluminum content, and further reduction in aluminum content brings about retardation in growth. Moreover, at the iron-rich edge of group (II), there is no region where few inclusions were formed like that between groups (I) and (II), and group (II) stretched smoothly to the inclusions shown in Photo. 2(d). However, in order to show the result of the area into which aluminum did not diffuse, Photo. 2(d) was taken at the symmetrical point of the reaction hole when the central axis of the cylindrical specimen was taken as the symmetrical axis. The inclusions in this photograph seem to be wüstite.

Next, the region where wüstite inclusions seemed to
be formed was investigated with respect to the segregation of oxygen, i.e. the distribution of wustite. In this case, there were no remarkable changes in the segregation in any parts of the specimens. Also, the specimens were checked from the viewpoint of the holding time of the specimen at the high temperature. In this case, the thickness of group (I) and the distance between groups (I) and (II) were detected to be almost constant regardless of the time, but the wustite inclusions shown in Photo. 2 (d) had a tendency to grow slightly with increase in holding time.

Next, the most interesting inclusions in the region shown in Photo. 2(b) were investigated by the microscope with a four hundred-fold magnification. At first the inclusions belonging to group (I) were observed. The results are shown in Photo. 3. Among these photographs, the inclusions shown in Photo. 3 (a) are especially worth noting. The inclusions formed a loop and the matrix was in the loop. What causes the formation of this type of inclusions is not yet known and must be further investigated. Photo. 3(d) shows the results on observations of the inclusions shown in Photo. 3(c) under cross nicols and points out that the inclusions contain alumina. Photo. 4 is the microscopic observation of the inclusions comprising group (II), where Photo. 4(b) represents Photo. 4(a) taken with cross nicols, and also indicates that there are some alumina inclusions.

Then, some inclusions comprising groups (I) and (II) were chosen at random and were analyzed by the microanalyzer. Whether the inclusions were alumina, spinel hercynite, or wustite was determined by using the methods detailed in the previous report(4). The results are shown in Table 1. There are many alumina inclusions among the inclusions comprising group (I), as shown in Photo. 3(d), but there are a considerable number of inclusions which seem to be spinel hercynite. On the other hand, the inclusions belonging to group (II), as shown in Photo. 4, were usually so small that microanalysis of them was difficult. The results show that there are many alumina inclusions in the relatively larger inclusions formed at about 1% aluminum content in the matrix. However, inclusions considered to be spinel hercynite and non-reacted wustite also seem to exist in group (II). Also, inclusions with the intermediate compositions which seem to be in the midst of the reaction, were contained in group (II).

V. Discussion

First, the regions where stratiform inclusions groups (I) and (II) were formed, were referred to the phase diagram. The equilibrium diagram of the iron-aluminum system is shown in Fig. 2(5). As our specimens also contain oxygen, strictly speaking, the ternary system should be referred to. However, since the oxygen content is much lower than the other two components, iron and aluminum, it was neglected. The diagram shows that a solid exists till the aluminum content is up to about 13% in the matrix and the

Table 1 EPXMA analysis of inclusions

<table>
<thead>
<tr>
<th>Size (μ)</th>
<th>Weight fraction in matrix (%)</th>
<th>Weight fraction in inclusions (%)</th>
<th>Judge</th>
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<tr>
<td></td>
<td>Fe</td>
<td>Al</td>
<td>Total</td>
</tr>
<tr>
<td>5</td>
<td>100</td>
<td>0.0300</td>
<td>100</td>
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<td>5</td>
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<tr>
<td>6.5</td>
<td>100</td>
<td>0.145</td>
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<td>100</td>
</tr>
<tr>
<td>6.3</td>
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<td>5.81</td>
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<tr>
<td>10</td>
<td>77.3</td>
<td>5.31</td>
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Photo. 4 Microphotographs of the inclusions formed in group (II) (non-etched, ×400/3/2)
liquid is at an aluminum content of more than about 20% at the experimental temperature, 1450°C. Thus, group (I) seems to be in the melt, and group (II) seems to exist in an α-solid solution.

Next, the experimental results were compared with the inner oxidation of solid metals with oxidizing gases, especially the inner oxidation of solid ferro-aluminum alloy with oxygen gas\(^{(6)}\)\(^{-}(12)\). This phenomenon has frequently been confirmed experimentally. There is, however, quantitative disagreement between the results, but the experiment leads to qualitative agreement. Obviously, a protective oxide layer formed consists of alumina, or, at least at high temperatures, of spinel hercynite, and iron ions diffuse through this layer, forming iron oxides at the surface. But the various oxidation layers are not clearly classified or defined. This phenomenon was compared with the analytical results shown in Table 1 from the viewpoint of the distribution of oxide, so that the distribution of the inclusions in the present work is very similar to that of oxide formed during the inner oxidation of the alloy, because there were some spinel hercynite inclusions in group (I) and many alumina inclusions in group (II). But there was a region between the stratiform groups (I) and (II) where few inclusions were formed in the present experimental results. Thus, the formation of groups (I) and (II), and the formation of the region between groups (I) and (II) where few inclusions were formed, were discussed. It is still unknown how the solubility of oxygen in solid alloys changes during the diffusion of aluminum into solid iron. However, if aluminum has the same effect on the solubility of oxygen in solid alloys as in liquid alloys as shown in Fig. 3, i.e., the solubility of oxygen is reduced when the aluminum content in the matrix is increased, until the aluminum content exceeds a certain critical point, and then the oxygen solubility begins to increase — then the microscopic observation on the distribution of the inclusions comprising group (II) can be satisfactorily explained. This idea is very reasonable especially in view of the experiment which was conducted by Kusano et al.\(^{(13)}\) in our laboratory and the fact that our experimental temperature was as high as that near the melting point. Kusano et al. measured the solubility of oxygen in δ-

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(9) W. Hessenbruch and W. Rohr : Heracs Vakumschmelze, (1923~33).
(10) N. A. Ziegeler : Trans. ASM, 100 (1932), 267.
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Fig. 6 Effect of chromium content in the melt on the distribution coefficient of oxygen.

iron and investigated the effect of chromium on the distribution coefficient of oxygen between solid iron and liquid iron. Figs. 4, 5, and 6 obtained by them show that when the chromium content in liquid iron is more than about 2.5%, the melting point reduces so slowly with the aluminum content that their experiment can be regarded as an isothermal one. Their experiments have also shown that when the chromium content in the liquid iron is more than about 3.5%, the solubility of oxygen is constant, but the distribution coefficient of oxygen between the solid and the liquid alloys still increases with increasing chromium content. Therefore, it can be concluded that the solubility of oxygen in solid alloy increases with increasing chromium content. Moreover, similarity between the activities in solid and in liquid has been reported on the solubility of sulfur in solid ferrosilicon alloy by Fielder (14) and others. Thus, it can be concluded that the solubility of oxygen in solid ferro-aluminum alloy changes similar to the behavior of the solubility of oxygen in liquid ferro-aluminum alloy as shown in Fig. 3. This allows a satisfactory explanation of the microscopic observation. On the other hand, what causes the formation of group (I) is still unknown. But, as group (I) existed in liquid region, according to Fig. 2, it may be suggested that the oxide layer is formed on the surfaces of iron and aluminum, even under a mild atmosphere because of the presence of water adsorbed in the surfaces, etc., before the melting of aluminum. This, however, is not certain and is a problem that needs further study.

VI. Summary

The present work was aimed at obtaining knowledge about the formation of inclusions after solidification, and so aluminum was diffused into solid iron containing oxygen at high temperature, and the behavior of the inclusions formed during the deoxidation was investigated. The results may be summarized as follows:

(1) The macroscopic observation shows that the inclusions formed distinguishable layers near the interface between liquid aluminum and solid iron.

(2) It is known from the microscopic observation of the interface that the inclusions are much smaller than those formed during the deoxidation of liquid iron with aluminum, and that the inclusions group consists of two stratiform inclusions groups. There was a region between the two stratiform groups where few inclusions were formed. The distribution of inclusions forming group (II) can be satisfactorily explained by the idea that the isothermal solubility of oxygen in solid ferro-aluminum alloy increases with increasing aluminum content, when it exceeds a certain content, i.e., on the basis of the discussion of the effect of chromium on the solubility of oxygen in solid ferro-chromium alloy.

(3) The inclusions belonging to group (I), where the aluminum content in the matrix is higher are larger than those belonging to group (II), and contain a special type of inclusions, such as loop type inclusions.

(4) The analytical results of the inclusions by the microanalyzer show that there are alumina and spinel hercynite in group (I), and that there are alumina, spinel hercynite, non-reacted wustite, and inclusions with intermediate compositions, which exist midway between the other two formations, in group (II), though they were usually so small that microanalysis of them was difficult.

(14) H. C. Fiedler : Trans. AIME, 239 (1967), 260.