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On the Alloy Layers Formed by the Reaction between Ferrous Alloys and Molten Aluminium*

By Mitsuo Niinomi** and Yoshisada Ueda***

Commercially pure Fe, Fe–Si, Fe–Cr, Fe–Ni, Fe–Mn, Fe–Cu and Fe–C alloys were dipped into molten aluminium (99.8 mass% Al) at 973, 1023 and 1073 K for various times. The alloy layers formed were examined by X-ray and EPMA analysis, and the hardness and thickness of the alloy layers were also measured. The alloy layer formed on each ferrous alloy is mainly composed of FeAl₃ and Fe₂Al₅, and much FeAl₁₃ is near the adhering aluminium and no FeAl₁₃ near the base metal. Fe₂Al₅ occupies the major portion of the alloy layer. For commercially pure Fe, Fe–Si, Fe–Cr, Fe–Ni and Fe–Mn alloys, the Fe–Al solid-solution exists inside the Fe₂Al₅ layer. The alloying elements in the base metal, especially Si, Ni and Cu, reduce the thickness of the alloy layers. The alloy layers formed on commercially pure Fe, Fe–Ni, Fe–Cr, Fe–Si, Fe–Mn and Fe–Cu alloys are tongue-like and that formed on Fe–C alloy is band-like. In the latter, however, a slightly tongue-like shape appears at a lower temperature. The hardness of each alloy layer near the base metal is higher than that near the adhering aluminium. The alloy layer formed on the Fe–C alloy is slightly harder than that on the other alloys.

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I. Introduction

Fe–Al alloy layers are formed instantly on ferrous alloys, when they are used in the parts contacting with molten aluminium. Then ferrous alloys begin to be attacked by molten aluminium. This problem has come to appear in an aluminium die casting mould for further mass production as well as in the holding-furnace of molten aluminium. It is a general practise at present that oxides such as Al₂O₃ or TiO₂ are produced on the surface of ferrous alloys in order to prevent the attack. However, there is a little difficulty in the adhesive ability of these oxides to ferrous alloys. Therefore, it is most desirable to improve the resistance of ferrous alloys against the molten aluminium.

It is necessary to clarify the dissolution process of ferrous alloys into molten aluminium in order to improve the resistance against molten aluminium. Furthermore, it is necessary to discuss the growth and chemical composition of the alloy layers formed by the reaction between various ferrous alloys and molten aluminium. In the present study the reactions between molten aluminium and commercially pure Fe, Fe–Si, Fe–Cr, Fe–Ni, Fe–Cu, Fe–Mn and Fe–C alloys are discussed.

II. Experimental Procedure

As commercially pure Fe, drawn φ8 mm rods were used. High purity pig iron for an Fe–C alloy and electrolytic pure iron for Fe–Si, Fe–Mn, Fe–Cr, Fe–Ni and Fe–Cu alloys were used respectively. Every alloy was melted in a Tamman furnace, alloying elements were regulated in 2–3 mass%, and the molten alloy was sucked up into a φ6–7 mm silica tube. All specimens were cut to about 50 mm in length. Fe–Si, Fe–Mn, Fe–Cr, Fe–Ni and Fe–Cu alloys were annealed in a vacuum for 10.8 ks (3 h) at 1273 K and furnace-cooled for homogenizing. These specimens were machined with a lathe, polished with #800 emery paper in order to produce 5 mm rods and employed as dipping specimens into molten aluminium. The chemical composition of the specimens is shown in Table 1. After degreasing with acetone, the specimens were dipped by constant 30 mm depth in the middle of a molten aluminium bath at 1073, 1023 and 973 K for fixed periods, and then took out and air-cooled. Commercially

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pure aluminium (nominal purity being 99.8%) was used as an Al-bath and was 0.35 kg for each dipping. The bath was prepared in a cylindrical graphite crucible which was about 45.1 mm in inside diameter, 140.6 mm in depth and 152.2 mm in height. A part about 10 mm long was cut out from the middle of dipping region of each specimen, and the thickness of the alloy layers was measured on its both ends. The sample layer was doubly etched with 3% Nital and 3% HF solutions, and its thickness was measured with a micrometer. For tongue-like alloy layers, the distance to the tips was averaged. Cylindrical samples were cut out from the remainder, smoothed by buffing and line-analyzed from the Fe-alloy matrix to the adhering aluminium by EPMA (accelerating voltage: 25 kV, incident X-ray angle: 15°). For the X-ray diffraction analysis, about 3 mm × 7 mm × 30 mm plates were dipped into molten aluminium, and parts about 3 mm × 7 mm × 10 mm in size were cut out from the dipped plates. Thereafter, the specimens were ground, step by step, with emery papers from the surface to the base metal and the alloy layers formed were analysed by X-rays. The analysis was performed on the surface, in the middle and near the base metal, using Co-radiation, Fe filter, the voltage of 30 kV and the current of 10 mA. The hardness of the alloy layers were measured by micro-Vicker’s hardness tester with 0.49 N load. The distance from the adhering aluminium to the indentation was also measured by an attached micrometer.

### III. Results and Discussion

1. **Composition of the alloy layers formed on each ferrous alloy**

Many studies of the alloy layers formed by the reaction between solid iron and molten aluminium have been carried out on aluminized steels, concerning mainly the effect of composition of molten aluminium bath on the alloy layers formed\(^{(1)}\)\(^{-}(3)\). These studies do not necessarily agree with one another in the composition of the alloy layers. However, the agreement can be seen in recent studies, in which pure iron or mild steel is dipped into molten pure aluminium\(^{(4)}\)\(^{-}(8)\) or into molten Al containing Si\(^{(2)}\). In the former, FeAl\(_3\) and Fe\(_2\)Al\(_5\) exist in order from the surface of the alloy layer to the base metal, and in the latter, the alloy layer is occupied almost by FeAl\(_3\).

The present investigation correspond to the former case and was carried out to confirm the above results and to examine the compositions of the alloy layers formed by the reaction between ferrous alloys and molten aluminium.

(1) **Fe–Al phase diagram**\(^{(9)}\)

According to the Fe–Al phase diagram\(^{(9)}\), various phases shown in Table 2 exist in different Fe concentrations (mass %) at room temperature under the equilibrium condition. Atomic ratios (Al/Fe) of FeAl\(_3\) and Fe\(_2\)Al\(_5\) phases are shown also in Table 2.
Table 2  Standard phases appearing in the Fe–Al phase diagram and their main atomic ratios.

<table>
<thead>
<tr>
<th>Fe concentration (mass %)</th>
<th>Phase</th>
<th>Atomic ratio (Al/Fe)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0–38.6</td>
<td>Al</td>
<td></td>
</tr>
<tr>
<td></td>
<td>FeAl</td>
<td></td>
</tr>
<tr>
<td>38.6–42.7</td>
<td>FeAl</td>
<td></td>
</tr>
<tr>
<td>42.7–44.3</td>
<td>FeAl</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fe₂Al₅</td>
<td></td>
</tr>
<tr>
<td>44.3–48.0</td>
<td>Fe₂Al₅</td>
<td></td>
</tr>
<tr>
<td>48.0–50.5</td>
<td>Fe₂Al₅</td>
<td></td>
</tr>
<tr>
<td></td>
<td>FeAl₂</td>
<td></td>
</tr>
<tr>
<td>50.5–67.0</td>
<td>FeAl₂</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fe–Al</td>
<td></td>
</tr>
<tr>
<td>67.0–100</td>
<td>Fe–Al</td>
<td></td>
</tr>
</tbody>
</table>

(2) Metallographic observations
Photograph 1 shows typical photographs of the alloy layers formed on commercially pure Fe, Fe–3Cu and Fe–2C alloys dipped at 1073 K. The alloy layers are markedly tongue-like except that of Fe–C alloy. For commercially pure Fe, the layer is most tongue-like and has many sharp tips. For Fe–Cr alloy, the layer has slightly lower sharpness in tip than that of commercially pure Fe. The same phenomena can be seen in Fe–3Ni and Fe–3Si alloys, but the thickness of the alloy layers is considerably thinner. The alloy layer formed on Fe–3Si alloy dipped at 973 K has more uniform tips than that at 1073 and 1023 K. The layers formed on Fe–2Mn and Fe–3Mn have short and wide tongue with many curved tips. Especially for Fe–2Mn alloy, the bottom of the alloy layer is more porous than that of other alloys. For Fe–3Cu alloy, the thickness of the alloy layer is considerably thinner and more uniform in the tip. For Fe–2C alloy, the layers formed at 1073 and 1023 K are band-like, and at 973 K slightly tongue-like. For Fe–3C alloy, the shape of the layer is also slightly tongue-like, and at 973 K similar to that for Fe–3Cu.

As shown in Photo. 2, a narrow Fe–Al solid-solution layer may exist inside of the tongue-like Fe₂Al₅ phase† at any temperature for commercially pure Fe, Fe–Si, Fe–Cr, Fe–Ni and Fe–Mn alloys. The solid-solution appears distinctly at 1073 K, but indistinctly at 973 K.

The growth of the solid-solution is remarkable for Fe–3Mn and especially for Fe–2Mn alloys. For Fe–C or Fe–Cu alloys, the solid-solution was not observed.

The solid-solution was identified by hardness measurement. The micro-Vicker’s hardness value with 0.245 N load was about Hv = 260 at the position where the solid-solution had sufficiently grown. The value is considerably lower than that of Fe₂Al₅ or FeAl₃ (mentioned later) and correspond to the hardness value of the solid-solution reported by Nishida et al.\(^{(12)}\).

In the case of mild steel and pure iron, FeAl₂ and the Fe–Al (Fe-rich) solid-solution have been reported to exist inside the Fe₂Al₅\(^{(10)}\). However, there is no report on the existence of FeAl₂, though many papers have reported the existence of the Fe–Al solid-solution\(^{(8),(10),(11)}\).

It is also considered that primary FeAl₃\(^{(13),(14)}\) exists in the adhering aluminium contacted with the alloy layer (Photo. 3).

Fe₃C remained in the alloy layers formed on Fe–3C alloy dipped at 973 K (Photo. 4), but was not observed at 1023 and 1073 K. The remaining of Fe₃C cannot be observed on Fe–2C alloy at any temperature.

Grains of the base metal in contact with the alloy layer were refined\(^{††}\), except in Fe–3Cu, Fe–2C and Fe–3C alloys (Photo. 5). This refinement is especially remarkable between tongue-like crystals. Obinata et al.\(^{(13)}\) reported that, when mild steel was dipped into molten aluminium, the base metal in contact with the alloy layer was decarburized and had coarsened grains at 973 K, but it was carburized and had refined grains at 1073 K. They attributed the cause of the grain refinement to the A₁ transformation. However, in the present work, the grain refinement was observed also at 973 K. Therefore, the refinement cannot necessarily be related to the A₁-transformation. It is concluded that, the grain refinement is caused by the internal stress in the iron grains in contact with the alloy layer, because aluminium dissolved into the base metal near the tongue-like layer increases the lattice constant of iron or

† Fe–Al solid-solution was defined by X-ray and EPMA analysis as mentioned later.

\(^{††}\) Grain refining is observed clearly in commercially pure iron and Fe–3Cr alloy.
Photo. 1 Typical photographs of the alloy layers.
(a) Commercially pure iron dipped for 3.6 ks at 1073 K. (b) Fe-3Cu alloy dipped for 3.6 ks at 1073 K. (c) Fe-2C alloy dipped for 3.6 ks at 1073 K (3% Nital etched and 3% HF etched).
(3) X-ray diffraction analysis of the alloy layer

Figure 1 shows X-ray diffraction patterns of the alloy layers formed on Fe–3Cr alloy. Similar patterns were obtained from the Fe–Al alloy layers formed on other ferrous alloys. The diffraction peaks were compared with ASTM data. Thus, from the surface of the alloy layers, (533) and (044) peaks$^\dagger$ of FeAl₃ appear near 45° and 52.5°, strong (002) peak of Fe₂Al₅ near 50°, weak (112) peak of Fe₂Al₅ near 54.5°. Analysing the alloy layers from the surface toward the base metal, (533) peak of FeAl₃ gradually disappears or falls down, and (004) peak of FeAl₃ is replaced by (110) peak of α-Fe. However, (002) peak of Fe₂Al₅ appears intensively at any position. It may be caused by anisotropic diffusion of Fe₂Al₅ reported by Heuman et al.$^{(11)}$ that any peaks other than (002) cannot be observed. Consequently, the X-ray diffraction results indicate that much FeAl₃ exists on the surface of the alloy layer and decreases in quantity with approach to the base iron.

![Diagram](image-url)

**Fig. 1** X-ray diffraction patterns (Fe–3Cr alloy dipped for 1.8 ks at 1073 K). (a) Surface of the alloy layer. (b) Center of the alloy layer. (c) The alloy layer near the base iron.

$^\dagger$ Peaks of Al may have some effect on these peaks.
base metal, resulting in the increased quantity of Fe$_2$Al$_5$ in the alloy layer and in the disappearance of FeAl$_3$ near the base metal.

(4) Hardness of the alloy layer

The hardness distribution of the alloy layers formed on various ferrous alloys is shown in Fig. 2. According to Nishida et al.,$^{12}$ the hardness of $\eta$(Fe$_2$Al$_5$) phase in Hv 870–1020, $\eta+\theta$(FeAl$_3$) phase Hv 670–870 and $\theta$ phase Hv 670–780. Comparing Fig. 2 with the results of Nishida et al.$^{12}$, the hardness of the alloy layers in the present work is similar to that of ($\theta+\eta$) phase. The hardness of the alloy layers has a tendency to become higher with approach to the base metal, and the effect of adhering aluminium may be considered in Fig. 2. Therefore, it is speculated that the phase in the surface of the alloy layers is lower in hardness than that in center. This phase may be estimated to be $\theta$ phase by referring to the hardness value, the X-ray diffraction pattern and the phase diagram.$^{9}$ According to Fig. 2, the hardness of the layer formed on Fe–3C alloy is slightly higher than those on the other alloys.$^5$ This phenomenon may be considered to be caused by the following reasons, though not yet certain:

(i) The alloy layers formed on the ferrous alloys except Fe–C are remarkably tongue-like (that on Fe–3Cu alloy is somewhat different), so that the hardness is lowered by the effect of the base metal.

(ii) The hardness of the alloy layer formed on Fe–C alloy is increased by the dissolution of a minute amount of C.

(iii) The hardness of the layer formed on Fe–C alloy is increased by the effect of retained Fe$_3$C.

(5) Composition of the alloy layer

determined by EPMA analysis

The Fe concentration (mass%) in the center of the alloy layers was measured by comparing EPMA X-ray intensity of Fe in the layers with Fe content in a standard FeAl$_3$ coexisting with Al in an Al–20 mass% Fe alloy. As the solubility of each alloying element in the alloy layers are adopted values shown below. Al concentration (mass%) in the center of the alloy layers was determined by subtracting the contents of Fe and soluble alloying elements from the total amount (100 mass%). Assuming that Fe in the alloy layer was substituted by the third element (M), (Fe$\cdot$M)/Al atomic ratio of the alloy layer was obtained. The results are shown in Tables 3 and 4. (Fe$\cdot$M)/Al atomic

<table>
<thead>
<tr>
<th>Specimens</th>
<th>Dipping time (ks)</th>
<th>Atomic ratio of (Fe$\cdot$M)/Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commercially pure iron</td>
<td>3.6</td>
<td>1:2.7</td>
</tr>
<tr>
<td>Fe–3Si</td>
<td>3.6</td>
<td>1:2.3</td>
</tr>
<tr>
<td>Fe–3Cr</td>
<td>0.9</td>
<td>1:2.5</td>
</tr>
<tr>
<td>Fe–3Ni</td>
<td>1.8</td>
<td>1:2.3</td>
</tr>
<tr>
<td>Fe–3Cu</td>
<td>1.8</td>
<td>1:2.2</td>
</tr>
<tr>
<td>Fe–2Mn</td>
<td>1.8</td>
<td>1:2.6</td>
</tr>
<tr>
<td>Fe–2C</td>
<td>1.8</td>
<td>1:2.9</td>
</tr>
<tr>
<td>Fe–3C</td>
<td>0.9</td>
<td>1:2.4</td>
</tr>
<tr>
<td>Fe–3C</td>
<td>1.8</td>
<td>1:2.5</td>
</tr>
</tbody>
</table>

Table 3 (Fe$\cdot$M)/Al atomic ratio of the alloy layer from EPMA analysis (1073 K).

<table>
<thead>
<tr>
<th>Specimens</th>
<th>Dipping time (ks)</th>
<th>Atomic ratio of (Fe$\cdot$M)/Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commercially pure iron</td>
<td>0.9</td>
<td>1:2.8</td>
</tr>
<tr>
<td>Fe–3Si</td>
<td>1.8</td>
<td>1:2.2</td>
</tr>
<tr>
<td>Fe–3Cr</td>
<td>1.8</td>
<td>1:2.2</td>
</tr>
<tr>
<td>Fe–3Ni</td>
<td>1.8</td>
<td>1:2.8</td>
</tr>
<tr>
<td>Fe–3Cu</td>
<td>1.8</td>
<td>1:2.7</td>
</tr>
<tr>
<td>Fe–2Mn</td>
<td>1.8</td>
<td>1:2.6</td>
</tr>
<tr>
<td>Fe–3C</td>
<td>1.8</td>
<td>1:2.4</td>
</tr>
</tbody>
</table>

Table 4 (Fe$\cdot$M)/Al atomic ratio of the alloy layer from EPMA analysis (973 K).
ratio ranges from 1:2.9 to 1:2.2 at 1073 K and from 1:2.8 to 1:2.2 at 973 K. These values are consistent with those shown in Table 2, which correspond to the compositions ranging from FeAl₃ to Fe₂Al₅. Many values are in the range of Fe₂Al₅.

It was reported by Tobe et al.⁷ that such an element as Ni or Cr is soluble in Fe₂Al₅ phase but insoluble in Al and FeAl₃ phases. The alloying elements dissolved to a certain extent into the Fe–Al alloy layers in the present experiment. Therefore, these layers are suggested to correspond with Fe₂Al₅ as reported by Tobe et al.⁷, from the results of EPMA analysis.

(6) Distribution of the third element in the alloy layers

The EPMA X-ray intensity distribution of each alloying element in the alloy layers is shown in Fig. 3. The solubility of each element was determined by comparing EPMA X-ray intensity with chemical analysis of the ferrous mother alloy. The solubility of every element into the alloy layer is lower than that into the iron matrix. The distribution of Cr and Mn is relatively even, but that of Ni is considerably irregular. Si is enriched in the interfaces of base metal/alloy layer and alloy layer/adhering aluminium. A ternary Fe–Al–Si compound may form in the Si-rich region, but the existence of the compound is not clarified and the above enrichment must be discussed further.

The above discussion on the alloy layers results in the conclusion that much FeAl₃ occupies the alloy layers near the adhering aluminium, the proportion of Fe₂Al₅ increases with approach to the base metal and FeAl₃ disappears near the base metal. Also, the hardness measurement and EPMA analysis indicate that Fe₂Al₅ exists over a wide range through the alloy layer. It is found that the Fe-rich Fe–Al solid-solution exists inside the Fe₂Al₅ phase of the alloy layer formed on ferrous alloys except Fe–C and Fe–3Cu.

2. Growth of the alloy layers

Figures 4–6 show the relation between thickness of the alloy layers and dipping time. These figures indicate that alloying elements in the base metal, especially Cu, Ni and Si, reduce the thickness of the alloy layers.

The thickness of the alloy layers increased generally with the dipping time, excluding the period after 1.8 ks (0.5 h) for Fe–2Mn alloy dipped at 1073 K and for Fe–3Mn at 1023 K. In any case, the growth rate of the alloy layer was rapid at the initial stage of dipping and became slower with time. The rate of thickening of the alloy layer formed on Fe–C alloys dipped for a long time was larger than that on the other alloys. In case of Fe–Mn alloys, for Fe–2Mn, the thickness decreased after 1.8 ks at 1073 K, and for Fe–3Mn, it was the thinnest at 1073 K and decreased after 1.8 ks at 1023 K.

Fig. 3 Results of EPMA analysis. (Fe–3Cr, Fe–3Cu, Fe–3Si, Fe–3Ni and Fe–2Mn alloys dipped for 1.8 ks at 1073 K).

Fig. 4 Relation between thickness of the alloy layer and dipping time (●○●—commercially pure iron, ▲△▲——Fe–2C, ■□■——Fe–3C).
According to the phase diagram\(^{(9)}\), Fe–2Mn alloy is a ferritic at 973 and 1023 K, and consists of a ferritic and an austenitic at 1073 K, and Fe–3Mn is ferritic at 973 K, and consists of a ferritic and an austenitic at 1023 and 1073 K. However, it cannot be concluded that the appearance of austenitic is responsible for the decrease of the thickness because the result of Fe–Mn alloys is in conflict with that of Fe–C alloys. S. Tobe et al.\(^{(7)}\) observed a similar result for SUS 304 alloy dipped into Al-bath at 1043 K and attributed it to the change in composition in the alloy layers with dipping time. This problem admits of discussion.

**IV. Conclusion**

Commercially pure Fe, Fe–C, Fe–Si, Fe–Mn, Fe–Cr, Fe–Ni and Fe–Cu alloys were dipped into molten aluminium. Fe–Al alloy layers formed by the reaction between ferrous alloys and molten aluminium were examined by metallography, X-ray diffraction, EPMA analysis and hardness measurements and discussed and the following results were obtained.

1. The alloy layers formed on each ferrous alloy have much FeAl\(_3\) near the adhering aluminium, and the proportion of Fe\(_2\)Al\(_3\) increases with approach to the base metal and no FeAl\(_3\) exists near the base metal. Fe\(_2\)Al\(_3\) exists over a wide range through the alloy layers. The Fe-rich Fe–Al solid-solution exists inside the Fe\(_2\)Al\(_3\) phase for the ferrous alloys except Fe–C and Fe–Cu alloys.

2. The alloying elements (C, Si, Cr, Ni, Mn and Cu) in the base metal reduce the thickness of the alloy layers, especially remarkably in the cases of Si, Ni and Cu.

3. The alloy layers formed on commercially pure Fe, Fe–Si, Fe–Cr, Fe–Ni, Fe–Mn and Fe–Cu alloys are tongue-like, and that formed on Fe–C alloy is band-like. In the latter, however, a slightly tongue-like shape appears at lower temperature of dipping.

4. The hardness of the alloy layers is lower near the adhering aluminium and higher near the base metal. The alloy layers formed on Fe–C alloy is slightly harder than that on the other alloys.

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**REFERENCES**

(14) A. Gierek und L. B. Kattowitz: Giesserei, 64 (1977), 391.