Determination of Aluminum Concentration in Molten Zinc by E.M.F. Method Using Calcium Fluoride Solid Electrolyte†

Shigeo Matsubara*, Tatsuhiro Tsutae*, Kazunari Nakamoto*, Iwao Katayama** and Takamichi Iida**

*Forming Technology Development Laboratories, Nisshin Steel Co., Ltd., 1 Tsurumachi, Amagasaki 660, Japan
**Faculty of Engineering, Osaka University, 2-1 Yamadaoka, Suita 565, Japan

Calcium fluoride solid electrolyte has been extensively used in galvanic cells for the measurement of fluorine potential to obtain the activity of alloys and compounds, because the ionic transference number of the electrolyte is about unity even at $P_F / P^0 = 10^{-6}$ above 550°C. So far there were no literature data available for the measurement below 500°C by use of the calcium fluoride solid electrolyte.

The purpose of this work is to develop the sensors for the control of aluminum concentration in a hot dip galvanizing bath, which is of industrial importance for producing high quality galvannealed steel sheets.

In this report, a trial has been made to measure the fluorine potential in a molten zinc bath artificially equilibrated with ZnF$_2$ at the temperatures between 450–500°C using CaF$_2$ cells with some kinds of reference electrode. By use of Bi, BiF$_3$ or Zn, ZnF$_2$ as the reference electrode, the cells respond quickly and stable emf values which agree fairly well with the literature data are obtained.

Subsequently, a trial has been made to measure the fluorine potential in molten Zn–Al baths artificially equilibrated with AlF$_3$ at the temperatures between 450–500°C using CaF$_2$ cells with the above reference electrodes. The initial response of these cells after immersion of the cells into these baths is relatively slow. However, once emf of the cell becomes stable, each cell responds quickly to the aluminum concentration change. The response time is not longer than 5 min. From the analysis of such emf measurements, the emf values are found to increase linearly with the logarithm of the aluminum concentration. The possibility of the present method has been ascertained in Zn–Al baths.

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Keywords: hot dip galvanizing, aluminum concentration, calcium fluoride solid electrolyte, reference electrode, fluorine potential, emf measurement, cell stability, zinc bath

I. Introduction

Control of the dissolved aluminum concentration in a hot dip galvanizing bath is of great importance for producing high quality galvannealed steel sheets. Nowadays, analysis by the fluorescence X-ray method for the specimen sampled from the bath has become popular to determine the aluminum concentration in the bath. However, this instrumental method takes a relatively long time and gives the concentration of total aluminum in stead of dissolved aluminum which has a major influence on the alloying performance of iron with zinc. In order to get a quality controlled galvannealed layer, a rapid and accurate method for determining this dissolved aluminum concentration has been required.

The authors have tried to apply the emf method using calcium fluoride (CaF$_2$) as solid electrolyte to the development of sensor for monitoring the aluminum concentration in a hot dip galvanizing bath.

The calcium fluoride solid electrolyte has been extensively used in galvanic cells for the measurement of fluorine potential to obtain the activity of alloys and compounds, because the ionic transference number of the electrolyte is about unity even at $P_F / P^0 = 10^{-6}$ above 550°C. So far there were no literature data available for the measurement below 500°C by use of the calcium fluoride solid electrolyte.

In this work, emf measurements have been carried out in a zinc bath artificially equilibrated with ZnF$_2$ at the temperatures between 450 and 500°C by using the calcium fluoride solid electrolyte and various reference electrodes to determine the optimum cell construction for the sensor. Then, emf measurements have been carried out in Zn–Al baths having an aluminum concentration of 0.01 – 1.674 mass% by using some of the most appropriate cells determined by the emf measurements in a zinc bath. The possibility of the present aluminum sensor using the calcium fluoride solid electrolyte has been experimentally studied.

II. Experimental Principles

When the following fluorine concentration cell $(-) P_F$ (I) $|$ CaF$_2$ | $P_F$ (II)(+)) is constructed using calcium fluoride as a solid electrolyte, the emf of the cell is represented by the following equation.

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\[
E = (1/2F) \int_{P_{F_3}(II)}^{P_{F_3}(I)} t_{\text{em}} d\mu_{F_3}
\]

Assuming that the transference number of fluorine in the solid electrolyte is nearly equal to unity, eq. (1) becomes

\[
E = (RT/2F) \ln \left( \frac{P_{F_3}(II)}{P_{F_3}(I)} \right)
\]

where \(E\) is the emf of cell, \(R\), the gas constant, \(T\), the thermodynamic temperature, \(F\), the Faraday constant, \(P_{F_3}\), fluorine pressure, and \(\mu_{F_3}\), chemical potential of fluorine.

When the mixture of Bi and BiF\(_3\) is used as a reference electrode, \(P_{F_3}(II)\) at a given temperature can be calculated from both eq. (3)\(^{(12)}\) and eq. (4).

\[
\Delta G^\circ (\text{BiF}_3) / \text{Jmol}^{-1} = -908750 + 236.7T/K
\]

\[
\Delta G^\circ (\text{BiF}_3) = -RT \ln \left( 1/P_{F_3}(II) \right)^{3/2}
\]

On the other hand, assuming that Zn–ZnF\(_2\) equilibrium is established between a molten zinc bath and ZnF\(_2\) powder packed into a silica tube mentioned hereafter, \(P_{F_3}(I)\) at a given temperature can be calculated in a similar way by eq. (5)\(^{(12)}\) and eq. (6).

\[
\Delta G^\circ (\text{ZnF}_2) / \text{Jmol}^{-1} = -762890 + 166.0T/K
\]

\[
\Delta G^\circ (\text{ZnF}_2) = -RT \ln (1/P_{F_3}(I))
\]

By substituting \(P_{F_3}(I)\) and \(P_{F_3}(II)\) in eq. (2), the emf of cell \(E\) is obtained as a function of the temperature and is represented by eq. (7).

\[
E_{\text{em}} = 813.9 - 0.00425T/K
\]

The cell emfs with other reference electrodes can be obtained by the same calculation procedure mentioned above. They are summarized in Table 1.

Assuming that the equilibrium relation Al + 3/2F\(_2\) (g) = AlF\(_3\) (s) is established between Zn–Al bath and AlF\(_3\) powder at the working electrode, the standard molar Gibbs energy of formation of AlF\(_3\) is given by eq. (8).

\[
\Delta G^\circ (\text{AlF}_3) = -RT \ln \left( a_{\text{AlF}_3} / (a_{\text{Al}})P_{F_3}(I)^{3/2} \right)
\]

Therefore, substitution of eq. (8) into eq. (2) gives

\[
E = (RT/3F) \ln a_{\text{Al}} - (RT/3F) \ln a_{\text{AlF}_3} - \Delta G^\circ (\text{AlF}_3)/3F + (RT/2F) \ln P_{F_3}(I)
\]

Here, the activity of AlF\(_3\) \(a_{\text{AlF}_3}\) may be regarded as unity. Also, assuming that Henry's law holds true with respect to the activity of aluminum \(a_{\text{Al}}\) since the concentration is quite low, eq. (9) can be rewritten as eq. (10) as a function of temperature and aluminum concentration.

\[
E = (2.303RT/3F) \log (\text{mass}%\text{Al}) + \text{const.}
\]

III. Experimental Procedures

1. Construction of calcium fluoride solid electrolyte cell

A CaF\(_2\) solid electrolyte crucible was prepared from a single crystal rod (Ohyo Koken Kogyo Co. Ltd., 10 mm diameter and 20 mm length) in which a hole (6 mm diameter, 18 mm depth) was made by drilling with the aid of a super sonic wave. Figure 1 shows a schematic representation of cell assembly devised in this study. Since this CaF\(_2\) solid electrolyte is immersed deeper than its length, the electrolyte is jointed with the silica tube of 5.5 mm in outside diameter and 500 mm in length using the zirconia cement as illustrated in Fig. 1. Another silica tube of 3.5 mm in outside diameter is inserted in the above-mentioned silica tube down to the height about 15 mm apart from the surface of reference electrode. To eliminate the oxidation of the reference electrode, commercial extra-high purity argon gas (\(>99.9999\) mass% purity) is supplied through this inner silica tube. Also, the outer cell made of silica which has an orifice of 3–4 mm in diameter has been devised and this outer cell is attached to the bottom of the electrolyte using the zirconia cement. The local equilibrium between a metal and its fluoride is established in this outer cell made of silica.

The experimental assembly is shown in Fig. 2. Molten zinc baths were prepared by melting the zinc ingots of

<table>
<thead>
<tr>
<th>Table 1</th>
<th>(\Delta G^\circ (J \cdot \text{mol}^{-1})) used in the present study.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Range (K)</td>
<td>Coexistence equation</td>
</tr>
<tr>
<td>298 ~ 1090</td>
<td>Zn + F(_2) = ZnF(_2)</td>
</tr>
<tr>
<td>298 ~ 922</td>
<td>Bi + 3/2F(_2) = BiF(_3)</td>
</tr>
<tr>
<td>298 ~ 1445</td>
<td>In + 3/2F(_2) = InF(_3)</td>
</tr>
<tr>
<td>298 ~ 1548</td>
<td>Al + 3/2F(_2) = AlF(_3)</td>
</tr>
</tbody>
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![Fig. 1 Schematic representation of the cell assembly.](image-url)
99.99 mass% purity in the graphite crucible in the air atmosphere. Zn–Al baths were obtained by melting the 99.99 mass% aluminum plate in 0.1 mm thickness in the above mentioned zinc bath by stirring the bath with an alumina rod. In some experimental runs, the possibility of reaction between aluminum in molten zinc and graphite was checked by using an alumina crucible instead of a graphite crucible.

Mixtures of Bi (m.p. 272°C), Zn (420°C), In (157°C) or Al (660°C) and their respective fluorides were chosen as the reference electrode material in view of the response and stability of cell. Bi, BiF₃ electrode was prepared by mixing Bi (99.99 mass% purity) and BiF₃ powder reagent (99.99 mass% purity) in a weight ratio of 10:1 put into the above mentioned calcium fluoride crucible. Zn, ZnF₂ and the other reference electrodes were prepared by a similar method described above. Tungsten wires of 99.97 mass% purity were used as lead wires for both working and reference electrodes because tungsten has been known to be stable for the corresponding molten metals below 600°C[13].

2. Measurement of cell EMF

Experimental procedures are as follows. K thermocouple for the bath temperature measurement and a lead wire for working electrode were preliminary immersed into the center of the bath at a given depth, respectively. A calcium fluoride solid electrolyte crucible was heated at the neighborhood of the bath temperature for about 10 min in the pre-heating furnace exposed to the air atmosphere before immersion into the bath. Before charging the calcium fluoride cell into the pre-heating furnace, the air in the silica tube, which was directly connected to the calcium fluoride solid electrolyte cell, was substituted by the argon gas. In addition, argon gas was supplied continuously during the emf measurement.

The emf of cell and the bath temperature around the calcium fluoride solid electrolyte crucible were recorded with the aid of a pen-recorder by way of an electrometer having an internal impedance of 10¹¹ Ω. These data were simultaneously memorized in an IC memory card. Such an operation enabled the use of personal computer to edit or analyze the data efficiently and to draw the emf vs. time graph easily after completing a series of experiments.

3. Analysis of the bath

After the cell emf reached an equilibrium value, the specimens for chemical analysis were sampled from the bath using a silica tube equipped with a suction syringe at its end. The specimen was cut off to be about 1 g and the silica tips remaining at its surface were removed. The specimen was then dissolved in 6N HNO₃ and its solution was submitted to I.C.P. spectrometry. The analysis was carried out on Al, Fe, Pb, Cd, Sn, Cu and Si in view of the use of graphite crucible for retaining the melt and minor impurity elements contained in zinc ingot or additive materials.

IV. Experimental Results and Discussion

1. Cell construction for molten zinc

In order to determine the optimum cell construction for the present sensor, emf measurements were carried out at first in a zinc bath artifically equilibrated with ZnF₂ by using a calcium fluoride solid electrolyte and various reference electrodes listed in Table 1. The ZnF₂ powder of 0.2 g was packed into the silica outer cell. The emf curves of cell with Bi, BiF₃ reference electrode are shown in Fig. 3. Each cell responds and shows relatively stable emf which agrees fairly well with the value calculated by eq. (7). Thus, reproducible measurements were possible and the scatter of stable emf in these experiments was about ±5 mV. Although the emf measurements were carried out under the condition that the experimental bath was opened to the air atmosphere, a considerably good agreement between measured and calculated values shows that there are no significant problems in emf measurements under an air atmosphere.

Emf measurements were carried out for the cell containing ZnF₂ in its silica outer cell between 0.1 – 1.0 g. When the ZnF₂ content in the outer cell is 1.0 g or 0.5 g, the cell emf would not become stable. A mass of ZnF₂ powder which is considered not to be equilibrated with molten zinc was found to remain at the outer bottom of CaF₂ solid electrolyte when the cell was overhauled after the emf measurement.

Thus, Zn–ZnF₂ equilibrium reaction at the outer bottom of the CaF₂ solid electrolyte is interfered and therefore the stable emf given by eq. (2) cannot be obtained when the ZnF₂ content is in excess.

When the ZnF₂ content is 0.1 g, nearly the same emf curve as in the case of 0.2 g was obtained. No detailed experiment was carried out on the lowest limit of the ZnF₂ content. In view of the life of a sensor, the higher ZnF₂
content seems to be better, because the ZnF₂ powder may flow out of the silica outer cell gradually due to the natural or forced convection in the zinc bath.

Figure 4 shows the emf of cell with the Bi, BiF₃ reference electrode as a function of temperature. The solid line shows the calculated value from the thermodynamic data given by eq. (3) and eq. (5). The difference between the calculated and measured value was a little larger at lower temperatures. However, the difference was not larger than 2 mV. This suggests that emf values measured in this study are approximately valid.

Subsequently, examples of emf curves of cell with the Zn, ZnF₂ reference electrode are shown in Fig. 5. In this case, since not only the reference electrode but also the working electrode is made from the Zn, ZnF₂, the calculated emf value becomes zero. It can been seen from Fig. 5 that the cell emf's measured are in good agreement with the calculated value. The initial response and the
emf fluctuation of cell with the Zn, ZnF₂ reference electrode were of the same order of those obtained with the Bi, BiF₃ reference electrode. Also, it was confirmed that the cell emf's measured were in the vicinity of zero between 450 and 500°C. It can be said, therefore, that the Zn, ZnF₂ is also suitable as a reference electrode of the present sensor.

The other reference electrodes were also investigated in the same way as mentioned above. In the case of In, InF₃, which is in the coexisting phase of liquid and solid at the measuring temperature, the stable emf was not obtained through a series of emf measurements. This may be due to the difference in the morphology of fluoride in the liquid reference electrode or the formation of InF[12], but no reliable data are available to explain this phenomenon.

On the other hand, when the reference electrode is made from Al, AlF₃, which exhibits the solid state at the measuring temperature, the cell emf would not become stable during the emf measurements in this study. This may be attributed to the difference in cell resistivity or oxidation of reference electrode materials. However, no detailed study on this point has been done.

2. Relationship between aluminum concentration in the bath and emf of cell with Bi, BiF₃ reference electrode

In each experiment, the aluminum concentration in the bath was increased stepwise by successive addition of the Al-10 mass%Al ingot into the bath. Since the bath was molten zinc which contained 0.01 ~ 1.674 mass% aluminum in this case, not the ZnF₂ powder but the AlF₃ powder of 0.2 g was packed into the silica outer cell. The Bi, BiF₃ or Zn, ZnF₂ was chosen as a reference electrode considering the results of preliminary experiments described in the previous section.

Examples of the emf curve of cell with the Bi, BiF₃ reference electrode obtained by such experiments at 450°C are shown in Fig. 6. This experiment was started with an aluminum concentration of 0.01 mass%. Since the abscissa of Fig. 6 represents the time at which the cell emf becomes stable, the initial response of cell is not shown. However, the stable emf's were obtained 4 ~ 5 h after the immersion of CaF₂ cell into the bath. Once the cell showed stable emf's, the cell responded quickly to the aluminum concentration change as can be seen from Fig. 6. The response time was not longer than 5 min. The cell responded similarly to the successive aluminum concentration change.

![Graph showing emf curve of cell with Bi, BiF₃ reference electrode.](https://via.placeholder.com/150)

**Fig. 6** Examples of the emf curve of cell: (W)⁡Zn-Al, AlF₃CaF₂Bi, BiF₃W(+) at 450°C.
At a given aluminum concentration, the cell showed relatively stable emf's within ±1 mV. Although the bath temperature fluctuated not more than ±5°C against the prescribed temperature (450°C), the corresponding fluctuation in cell emf was not found from the emf measurements. Figure 7 depicts the result of another experimental run. Figure 8 shows the relationship between the aluminum concentration and the cell emf measured in a series of experiments at 450°C. Each symbol denotes its corresponding result of cell emf. In any case, the cell emf linearly increased with an increase in the logarithm of aluminum concentration. However, the cell emf fluctuated within the range of ±20 mV at the same aluminum concentration level. As already described in chapter 2, the inclination is calculated to be 47.8 at 450°C by assuming that the equilibrium relation \( Al + \frac{3}{2}F_2 (g) = AlF_3 (s) \) is established between the Zn-Al bath and AlF_3 powder at the working electrode and that \( a_{AlF_3} \) is unity and the Henry's law holds true with respect to the activity of aluminum \( a_{Al} \). On the other hand, the inclination of experimental results ranged from 36 to 58. The response of cell emf to the aluminum concentration change was not necessarily reproducible. This may be attributed to the difference between the aluminum concentration at the working electrode and that of the bulk of the bath in each experiment. However, no detailed study on this point has been done because it is impossible to analyze the aluminum concentration at the working electrode.
correctly. Generally, the life of cell was not shorter than 100 h.

In the case of an alumina crucible, nearly the same results were obtained as those in the case of a graphite crucible. This suggests that there is little possibility of reaction between the graphite and aluminum in the bath.

3. Relationship between aluminum concentration in the bath and emf of cell with Zn, ZnF\(_2\) reference electrode

An example of the emf curve of cell with Zn, ZnF\(_2\) reference electrode at 450°C is shown in Fig. 9. The stable emf was obtained 4 - 5 h after the immersion of CaF\(_2\) cell into the bath and the response time against the aluminum concentration change was not longer than 5 min. Similar results to those in the case of the Bi, BiF\(_3\) reference electrode were obtained in this case, too. Figure 10 depicts the relationship between the aluminum concentration and the cell emf in Fig. 9. It is obvious from Fig. 10 that the cell emf linearly increases with an increase in the logarithm of aluminum concentration. The inclination of experimental results was 52.8, whereas that calculated was 47.8 at 450°C.

As far as the life of the cell is concerned, there was no significant difference between the cells with the Bi, BiF\(_3\) reference electrode and the Zn, ZnF\(_2\) reference electrode.

4. Comparison of fluorine pressure between two reference electrodes

To judge the validity of these measurements, the fluorine pressure \(P_F\) in Zn-Al baths was calculated by the following procedures using emf data for both reference electrodes. In the case of the Bi, BiF\(_3\) reference electrode, from Nernst's equation represented by eq. (2) and eqs. (3) and (4), the fluorine pressure at the working electrode \(P_F\),\(\text{II}\) can be obtained by substituting the values of \(E\) and \(T\) into these equations. The calculated values of \(P_F\),\(\text{II}\) are plotted against the aluminum concentration using the value of \(E\) obtained experimentally. In the case of the Zn, ZnF\(_2\) reference electrode, \(P_F\),\(\text{II}\) was calculated by substituting eqs. (5) and (6) into eq. (2).

As a result values of \(P_F\),\(\text{II}\) at 450°C as well as 500°C for both reference electrodes were in good agreement each other as shown in Fig. 11 when they are compared at the same aluminum concentration level. This suggests that emf values measured in this study for both reference electrodes are approximately valid.

This result also shows that the steady emf can be obtained by the present calcium fluoride solid electrolyte cell down to about \(P_F/\text{Pa}=10^{-57}\) above 450°C and \(P_F/\text{Pa}=10^{-53}\) above 500°C. In view of the report that the ion transfer number of the calcium fluoride solid electrolyte is about unity at \(P_F/\text{Pa}=10^{-62}\) above 550°C\(^{10}\), the ion transfer number in the present experimental conditions may be taken as about unity.

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**Fig. 9** Example of the emf curve of cell: (--)W|Zn-Al, AlF\(_3\)|CaF\(_2\)|Zn, ZnF\(_2\)|W(+) at 450°C.

**Fig. 10** Relationship between the aluminum concentration in Zn-Al baths and the emf of cell: (--)W|Zn-Al, AlF\(_3\)|CaF\(_2\)|Zn, ZnF\(_2\)|W(+) at 450°C.
V. Conclusions

As a means for in situ measurement of aluminum concentration in a hot dip galvanizing bath, a sensor based on the emf method using the calcium fluoride solid electrolyte has been studied. In this report, a trial has been made to measure the fluorine potential in molten Zn or Zn-Al baths artificially equilibrated with ZnF₂ or AlF₃ at the temperature between 450 – 500°C using CaF₂ cells with different kinds of reference electrodes. The summary of the results is as follows.

1. By use of Bi, BiF₃ or Zn, ZnF₂ as the reference electrode, the cells responded quickly and stable emf values which agreed fairly well with the literature data were obtained in the experiment using a molten Zn bath.

2. In the case of In, InF₃, the stable emf was not obtained through a series of emf measurements, whereas this reference electrode is in the coexisting phase of liquid and solid at the measuring temperature. When the reference electrode is made from Al, AlF₃, which exhibits the solid state at the measuring temperature, the cell emf would not become stable during the emf measurements in this study.

3. It was found that the following cells: (–)W|Zn-Al, AlF₃|CaF₂|Bi, BiF₃|W(+) and (–)W|Zn-Al, AlF₃|CaF₂|Zn, ZnF₂|W(+) responded within 5 min to the successive aluminum concentration change and showed the stable emf which increased linearly with an increase in the logarithm of aluminum concentration.

4. The values of \( P_{F_2}(\text{II}) \) calculated from the experimental data at 450°C as well as 500°C for both Bi, BiF₃ and Zn, ZnF₂ reference electrodes were in good agreement each other when they were compared at the same aluminum concentration level. This suggests that emf values measured in this study for both reference electrodes are approximately valid.

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