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# The control of inclusion composition to prevent the rust formation for ferritic stainless steel

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In recent years, the amount of ferritic stainless steel production has increased. However, the rust formation by the salt spray test was pointed out in the past. At the centre of the circular rust zone, pitting corrosion where water-soluble nonmetallic inclusions were embedded was observed. These inclusions originated from the suspended refining slag and consisted of multi-phase oxides and sulphides.

By the experiments and thermodynamic consideration of the water-solubility, not only CaO or CaS, but also lime rich calcium-aluminates or calcium-silicates have shown large water-solubility. The composition of oxide phase in the inclusions was almost the same among the samples from molten steel, slab, or cold rolled sheet. On the contrary, CaS was clearly observed around the oxide in the sample of cold rolled sheet, although it was not found in the molten steel or slab samples. The enrichment of sulphur occurred from the desulphurization reaction of the suspended slag particles in the molten steel and also occurred from the diffusion of sulphur to the oxide inclusions during the heating of the slab. The optimization of refining slag composition has lead to produce the ferritic stainless steel without rust formation.

Keywords: stainless steel, rust, calcium aluminates, calcium sulphides, water-solubility, refining slag, composition control of inclusions.

## Introduction

In recent years, the amount of ferritic stainless steel production mainly for the automotive field has increased. The annual production of ferritic stainless steel sheet and coil by Nippon Steel Corporation has reached about 200 thousand tonnes, which is comparable to that of austenitic stainless steel. Through the development of refining techniques, extra low carbon ferritic stainless steels with improved formability, corrosion resistance, weldability etc. has been possible to provide at low cost.

However, rust formation by the salt spray test was pointed out[1–2]. In previous researches, the pitting corrosion was observed at the centre of the circular rust zone. The water-soluble inclusions, which consisted of multi-phase oxides and sulphides, have known to cause the pitting corrosion. As these inclusions originated from the suspended slag particles, the control of refining slag composition is important. Nevertheless, the knowledge of the water-solubility and the formation mechanism of each oxide or sulphide were not enough. In this paper, the experiments and thermodynamic considerations about the water-solubility of the inclusions have been carried out, and the changing mechanism from the refining slag to the water-soluble inclusion was discussed.

### Process of producing ferritic stainless steel

Figure 1 shows the process of producing ferritic stainless steel at Nippon Steel Corporation. Steelmaking and hot rolling mills are located at the Yawata works and hot coils are transported to the Hikari works by ship about 100 km where the cold rolling mill is located. The steelmaking process in Yawata works is also shown in Figure 1. Hot metal from the blast furnace is dephosphorized by the hot metal pretreatment process. Crude decarburization and the addition of ferrochromium alloy are achieved by the top and bottom blowing converter. Final decarburization is carried out by the vacuum treatment equipment (VOD or SUS-REDA[3]). After the deoxidation and the composition adjustment, molten steel is cast in a continuous casting process to make slabs. These slabs are rolled to the hot coils and transported to Hikari works. At the Hikari works, after the cold rolling, final products are finished through annealing and pickling lines or bright annealing lines.

## Nonmetallic inclusions at the centre of rust

The rust formation test is carried out by spraying the 5 weight per cent NaCl dissolved water at 333 K onto the stainless steel sheet (salt spray test). At the centre of the rust circle, nonmetallic inclusions can be observed as depicted in Figure 2. The quantitative analysis by EPMA has clarified that the inclusion consists of multi-phase oxides and sulphides. The oxide phase consists of Ca, Al, Si,and Mg. The sulphide phase is mainly CaS. The rust would be caused by the destruction of the passive film where the water-soluble phases of the inclusion were dissolved.

## Water-solubility of oxides and sulphide

To investigate the water-solubility, 1g/l each of oxide and sulphide powder was immersed into the 5 weight per cent NaCl dissolved water at 333 K for 240 min., and the change in the weight was measured. The mixtures of two or three oxides were synthesized by the reagents in a Pt crucible. Table I summarizes the experimental results, where the

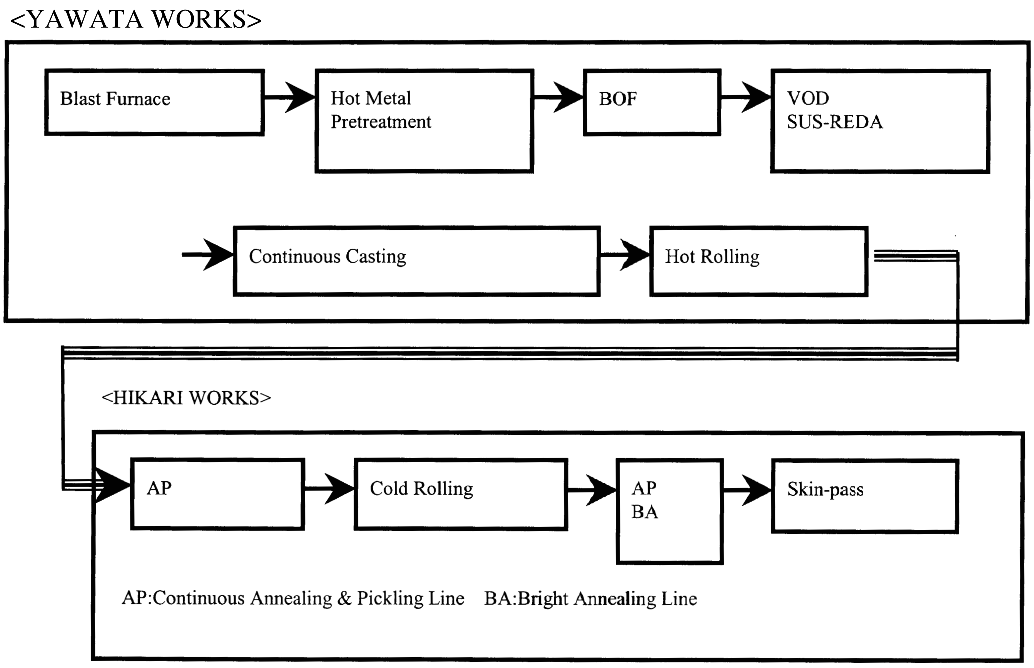

**Figure 1. The process of producing ferritic stainless steel at Nippon Steel Corporation**

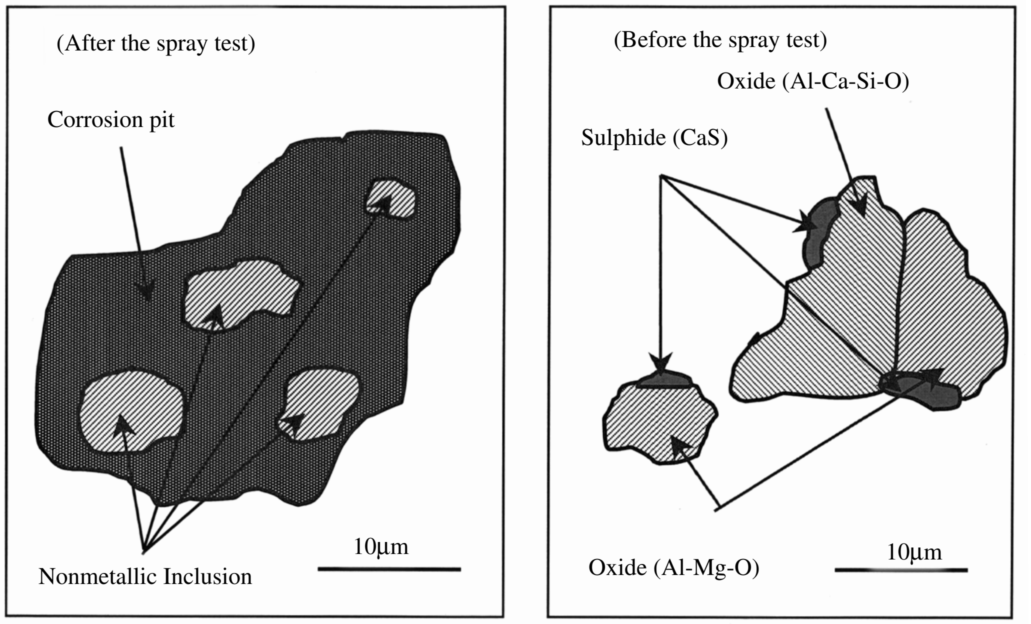

**Figure 2. Schematic representation of rust and nonmetallic inclusions**

**Table I**
**Water-solubility of various oxides and sulphides**

| | Weight loss through water immersion (%) |
|---|---|
| CaS (reagent) | 37.4 |
| CaO (reagent) | 84.0 |
| $Al_2O_3$ (reagent) | 0.0 |
| $3CaO{\cdot}Al_2O_3$* | 13.4 |
| $12CaO{\cdot}7Al_2O_3$* | 7.4 |
| $CaO{\cdot}Al_2O_3$* | 14.4 |
| $CaO{\cdot}Al_2O_3$ with 0.5% MgO* | 16.0 |
| $CaO{\cdot}Al_2O_3$ with 5% $SiO_2$* | 2.0 |

*compound made by reagents

water-solubility is shown as the degree of weight loss in weight per cent. Not only CaO or CaS, but also $3CaO{\cdot}Al_2O_3$ or $CaO{\cdot}Al_2O_3$ have revealed large water-solubility. On the other hand, the mixture of $CaO{\cdot}Al_2O_3$ and 5 weight per cent $SiO_2$ has decreased the water-solubility significantly.

The thermodynamic calculation was carried out. The considered chemical reactions are summarized in Table II. The solubility or solubility product of each ion can be obtained by the standard free energy[4]. In these calculations, the anion, which has the largest solubility in each pH region, was used and the activity of oxide, sulphide, $H_2O$ and $H_2S$ were regarded as one.

**Table II**
**Considered chemical reactions and their standard free energy**

|  |  | (kJ/mol) |
|---|---|---|
| $CaO + 2H^+ = Ca^{2+} + H_2O$ | $\Delta G°_{298} = -186.7$ | [1] |
| $Ca(OH)_2 + 2H^+ = Ca^{2+} + 2H_2O$ | $\Delta G°_{298} = -129.3$ | [2] |
| $SiO_2 + H_2O = H_2SiO_3$ | $\Delta G°_{298} = +17.2$ | [3] |
| $Al_2O_3 + H_2O = 2AlO^{2-} + 2H^+$ | $\Delta G°_{298} = +174.4$ | [4] |
| $CaS + 2H^+ = Ca^{2+} + H_2S$ | $\Delta G°_{298} = -104$ | [5] |
| $MnS + 2H^+ = Mn^{2+} + H_2S$ | $\Delta G°_{298} = -37.5$ | [6] |
| $FeS + 2H^+ = Fe^{2+} + H_2S$ | $\Delta G°_{298} = -6.33$ | [7] |
| $3CaO·Al_2O_3 + 4H^+ = 3Ca^{2+} + 2AlO^{2-} + 2H_2O$ | $\Delta G°_{298} = -372.6$ | [8] |
| $CaO·Al_2O_3 = Ca^{2+} + 2AlO^{2-}$ | $\Delta G°_{298} = +8.66$ | [9] |
| $CaO·2Al_2O_3 + H_2O = Ca^{2+} + 4AlO^{2-} + 2H^+$ | $\Delta G°_{298} = +1532.6$ | [10] |
| $2CaO·SiO_2 + 4H^+ = 2Ca^{2+} + H_2SiO_3 + H_2O$ | $\Delta G°_{298} = -229.8$ | [11] |
| $CaO·SiO_2 + 2H^+ = Ca^{2+} + H_2SiO_3$ | $\Delta G°_{298} = -80.1$ | [12] |

Figure 3 shows the solubility of each oxide, hydroxide and sulphide. CaO, $Ca(OH)_2$ and CaS have large solubility, although $Al_2O_3$, $SiO_2$, MnS or FeS can scarcely dissolve in the water. The solubility products of many composite oxides are shown in Figure 4. The lime rich calcium-aluminates as $3CaO·Al_2O_3$, $CaO·Al_2O_3$ and the lime rich calcium-silicates as $2CaO·SiO_2$, $CaO·SiO_2$ show large solubility. These calculations have good agreement with the experimental results. By the phase diagram, the mixture of $CaO·Al_2O_3$ and 5 weight per cent $SiO_2$, which shows poor solubility, decompose to $CaO·Al_2O_3$, $CaO·2Al_2O_3$ and $3CaO·2SiO_2$ phases at RT. It can be considered that the decrease of the $CaO·Al_2O_3$ content or the decrease of lime activity would lower the water-solubility.

These results suggest that the CaS and the lime rich calcium-aluminate phases in Figure 2 have caused the pitting corrosion. The prevention to form these phases would be the measures against the rust formation.

## Changing mechanism from the refining slag to the water-soluble inclusions

Typical inclusions of the following samples were investigated by EPMA:

- Cross-sectional area of dip-up sample from the molten steel in TD
- Cross-sectional area of CC slab
- Surface of the cold rolled sheet.

Characteristic X-ray images of Al, Mg, Ca, S, and O were observed. The average composition of the inclusions, which consist of many phases, was estimated with the quantitative analysis results and the volume fraction of each phase. Results are summarized in Photo.1.

In every case, the oxide phase consisted of CaO, $Al_2O_3$ and MgO. According to the quantitative analysis, the composition of the oxide phase was almost the same in each sample. This kind of oxide would originate from the refining slag. To control the oxide in poor water-soluble characteristics, the precise control of the refining slag composition is important.

On the other hand, CaS was clearly observed around the oxide in the sample of cold rolled sheet, although it was not found in the molten steel or slab samples. As shown in Figure 5, the average concentrations of sulphur and $Al_2O_3$ in the inclusions sampled from molten steel were higher compared with the refining slag composition. These results show that the sulphur content increases from the refining slag to the inclusions in molten steel, and is more entiched in the inclusions in cold rolled sheet.

To consider the mechanism of sulphur enrichment from the refining slag to the inclusions, the equilibrium partition ratio of sulphur was considered. In Figure 6, the sulphur partition ratio of the refining slag and the inclusions in molten steel are compared with the equilibrium values of $CaO-Al_2O_3$ flux[4]. The sulphur content of the refining slag is much lower than the equilibrium. Even though the content of $Al_2O_3$ increases through the collision with the deoxidation products, desulphurization capacity of the

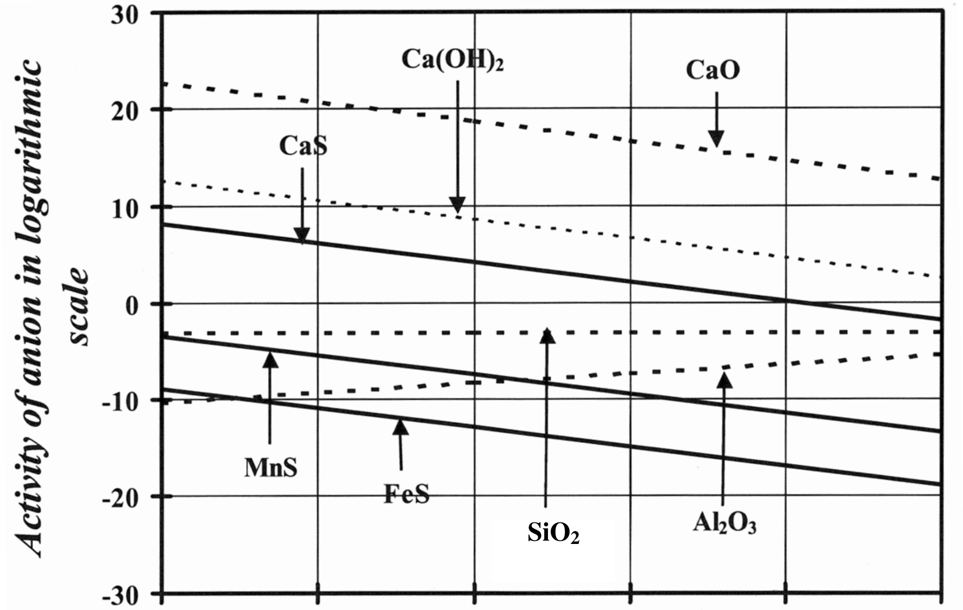

Figure 3. Solubility of each oxide, hydroxide, and sulphide

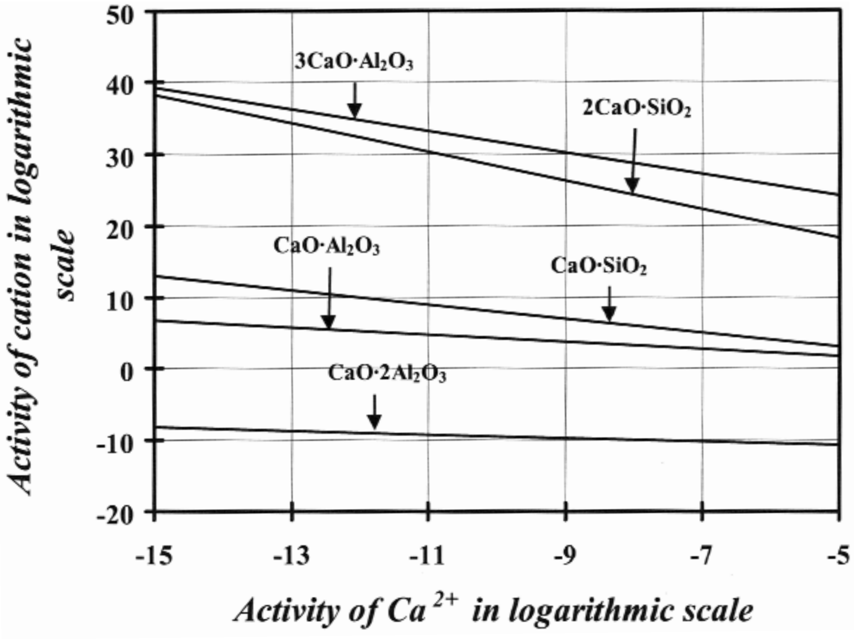

**Figure 4. Solubility product of each composite oxide**

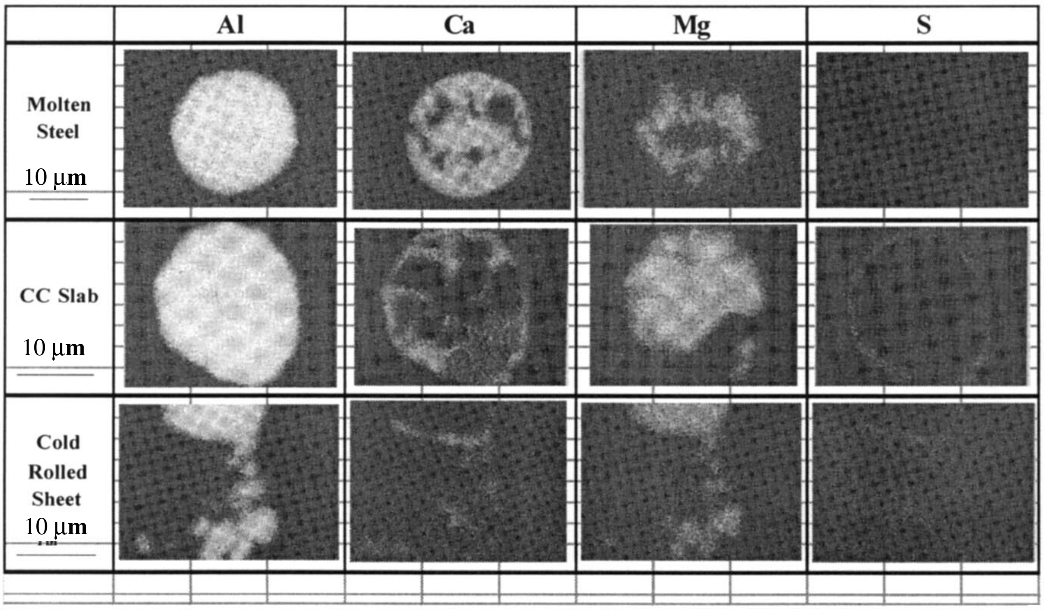

**Photo 1. Typical inclusions observed in the molten steel, CC slab, and cold rolled sheet**

inclusion is high enough. It can be considered that the suspended slag particles, which have high desulphurization capacity and a large reaction interfacial area, adsorb sulphur from the molten steel and get close to the equilibrium condition.

As the mechanism of the sulphur enrichment to the inclusions of cold rolled sheet, the effect of heat treatment was considered. To confirm this mechanism, metal samples from the molten steel were heated to 1273 K for 3 hours, which corresponds to the heating temperature of the slab before hot rolling. The observed results before the heat treatment and after the heat treatment are summarized in Photo 2. Sulphur enrichment around the oxide phase can be clearly observed. As the oxide inclusion has a high desulphurization capacity, the activity of sulphur in the oxide phase would be much lower than that in metal. Then, the diffusion of sulphur to the oxide during the heating can take place and cause sulphur enrichment. In this experiment, the precipitation of CaS was not observed, although the solubility of sulphur in the oxide phase would be small in the RT. Because of the high cooling rate in this experiment, sulphur could be dissolved in the oxide phase in a supersaturated condition. In industry, as the cooling rate is low, CaS would be precipitated from the oxide phase.

To prevent the precipitation of the water-soluble CaS, lowering the desulphurization capacity of the oxide phase is as important as the lowering the sulphur content in slag.

## Measures to prevent rust formation

To prevent the formation of water-soluble oxides or sulphides, composition control of inclusions is very

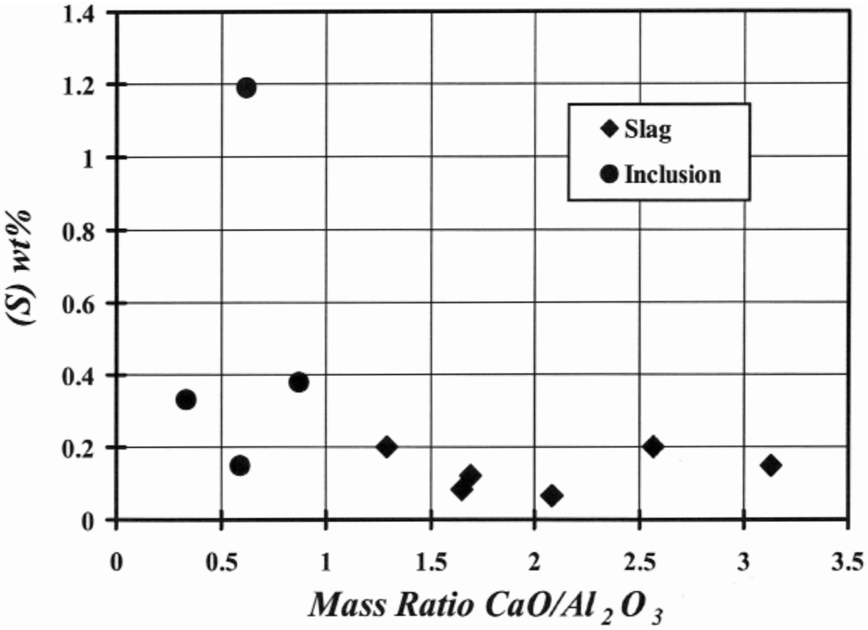

Figure 5. Difference of sulphur and $Al_2O_3$ contents between refining slag and inclusions

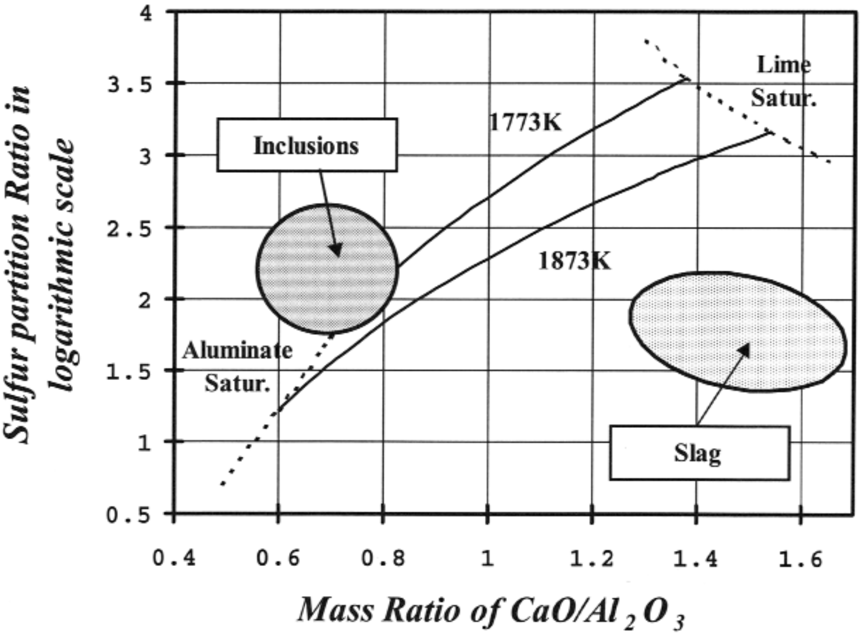

Figure 6. Comparison of sulphur partition ratio to the equilibrium value

important. As these inclusions originated from the suspended refining slag, the control of refining slag composition is the only effective technique.

The first step is to lower the sulphur content in slag which lower the sulphur content of the inclusions and prevents the formation of CaS. The second step is to lower the CaO content in slag, which can prevent the formation of lime rich calcium-aluminate inclusions. The third step is to lower the deoxidation degree, which can increase the $SiO_2$ content of the inclusions. By the second and third step, the inclusion composition can be changed to decrease the water-solubility and also to decrease the sulfide capacity. By the application of these measures, Nippon Steel can produce ferritic stainless steel without rust formation.

## Conclusions

To prevent the formation of water-soluble inclusions, which cause rust on the ferritic stainless steel surface, the water-solubility of the inclusions and the changing mechanism from the refining slag to the water-soluble inclusions have been discussed. The results are summarized as the followings:

- According to the experiments and thermodynamic consideration of the water-solubility of the inclusions, not only CaO or CaS, but also lime rich calcium-aluminates ($3CaO{\cdot}Al_2O_3$, $CaO{\cdot}Al_2O_3$) or calcium-silicates ($2CaO{\cdot}SiO_2$, $CaO{\cdot}SiO_2$) have shown large water-solubility. The mixture of $CaO{\cdot}Al_2O_3$ and 5 weight per cent $SiO_2$ has decreased the solubility significantly.

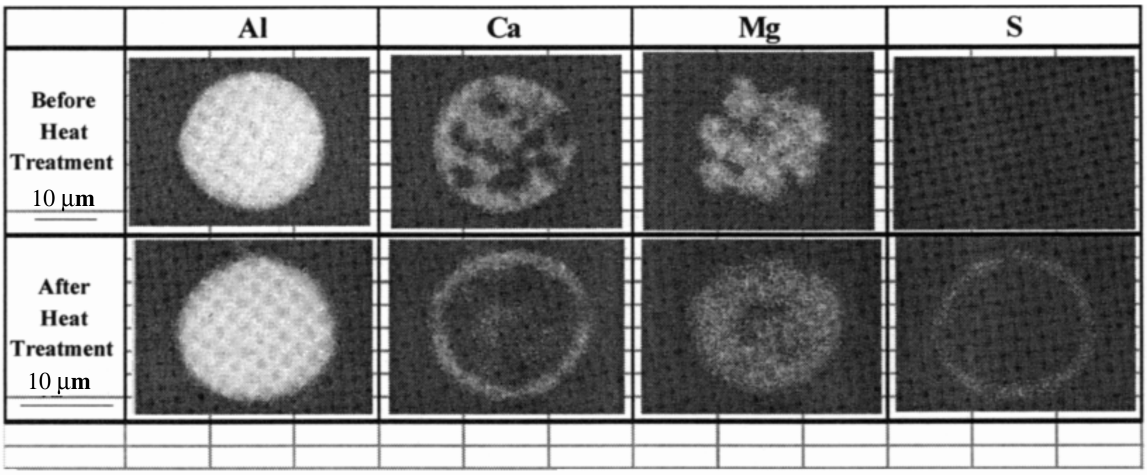

**Photo 2. The composition change of inclusions through heat treatment**

- The composition of the oxide phase in the inclusions was almost the same among the samples from molten steel, slab, or cold rolled sheet. This kind of oxide would be originate from refining slag. To control the oxide in poor water-soluble characteristics, the precise control of the refining slag composition is important.
- CaS phase has been clearly observed around the oxides in the sample of cold rolled sheet, although it was not found in the molten steel or slab samples. Compared of the refining slag compositionwith the average inclusion composition in molten steel, sulphur and $Al_2O_3$ have been entiched. The enrichment of sulphur in the inclusion would occur through the desulphurization reaction of the suspended slag particles in the molten steel.
- Sulphur enrichment around the oxide phase has been clearly observed in the metal samples obtained from the molten steel in TD after heating in high temperature. The enrichment of sulphur would occur through the diffusion of sulphur to the oxide inclusion during the heating of the slab. After cooling, water-soluble CaS would be precipitated around the oxide phase.

By controlling the refining of the slag composition based on this knowledge, the ferritic stainless steel without rust formation can be produced.

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