INVESTIGATION OF THE CORROSION MECHANISM OF Al_2O_3-ZrO_2-C SLIDE GATE PLATES FOR THE CASTING OF Ca-ADDED STEEL

Yuichi Kato[1], Tadashi Ikemoto[1], Kiyoshi Goto[1]

[1]Nippon Steel & Sumitomo Metal Corporation, Futtsu, Japan

ABSTRACT

It is known that the addition of calcium (Ca) to the steel is effective for preventing the clogging because Ca reacts with alumina inclusions, forming calcium aluminates, which have low melting points and do not form precipitated layers. However, it was observed that the corrosion of Al_2O_3-ZrO_2-C (AZC) slide gate plates increased when they are used for Ca-added steel casting. Therefore, it became necessary to improve the corrosion resistance of the AZC slide gate plates. Based on the microscopic observation of used AZC slide gate plates, it became clear that when these slide gate plates were used for casting Ca-added steel, they developed many more pores than the original material, and calcium aluminates penetrated into the slide gate plate structure, along the pores. It was considered that because more pores developed in the structure, the corrosion of the AZC slide gate plates was accelerated. To clarify the mechanism of the porosity increase of the AZC slide gate plate structure, the gas generation from the refractory materials was thermodynamically investigated. Thermodynamic calculations were conducted for the condition where solid state Al_2O_3, ZrO_2, mullite and C, which are components of the AZC slide gates, coexisted with pure Fe or Fe-Ca in the liquid condition at 1823K (1550 ^oC). The analysis indicated that the partial pressure of SiO gas generated in the slide gate plate material, when used with Ca-added steel, was much higher than for other steels. Therefore, it was suggested that it is necessary to suppress the gas generation from the slide gate plate materials, to maintain the dense structure, and improve the corrosion resistance of the AZC slide gate plates. So experimental refractory samples containing CA6 aggregate, for suppressing the SiO gas generation, were prepared. As a result of corrosion test, corrosion resistance of the sample material was 30% better than the conventional AZC slide gate material.

INTRODUCTION

A continuous casting facility includes a long nozzle, tundish refractories, slide gate plates and submerged entry nozzles, as shown in Figure 1. Because the refractories for continuous casting are used in the last stage of the steelmaking process, the stability and the durability of the refractories affects the productivity of the continuous casting operation and the steel quality. Therefore, clarifying the wear mechanism of the refractories for continuous casting is very important not only for improving the lifetime of the refractories but also for improving the steelmaking process.

Slide gate plates are one of the functional refractories. They are used for controlling the flow rate of steel i.e. from the tundish to the mold. Figure 2 shows a schematic view of a slide gate plate. Slide gate plates consist of two or three plates, which have a central hole that is the channel for steel flow. By sliding one plate and shifting the position of the central hole, the slide gate plate can control the flow rate of the steel.

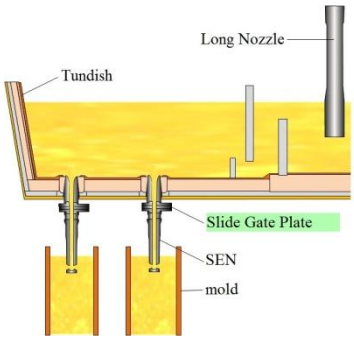

Fig.1: Schematic image of the refractories for continuous casting

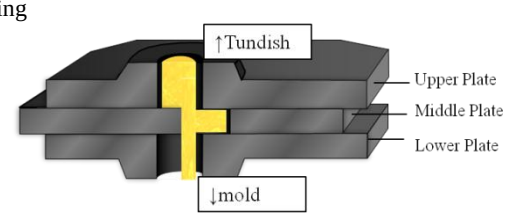

Fig.2: Schematic view of slide gate plates

Figure 3 shows the working surface of the middle plate after use. The forms of wear are the change of the inner hole diameter by corrosion, the surface abrasion by the metal stream, and the thermal spalling cracks. The life time of the slide gate plate is determined, especially by the diameter change of the inner hole by corrosion and/or thermal spalling. So the slide gate plate needs to have balanced properties for corrosion resistance against molten steel and molten oxides, and good thermal spalling resistance.

To satisfy these required properties, the slide gate plates have so far, mainly consisted of Al_2O_3 aggregate, ZrO_2-mullite aggregate, and Al_2O_3-ZrO_2 aggregate, along with phenol binder.

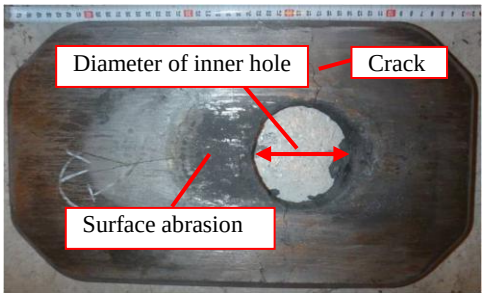

Fig.3: Working surface of the middle plate after use

On the other hand, the clogging of a submerged entry nozzle (SEN) caused by the alumina inclusions that precipitate from steel, is a serious problem for the continuous casting

operation and the steel quality. It is known that the addition of Ca to the steel is effective for preventing the clogging because Ca reacts with alumina inclusions and forms low melting point calcium aluminates, which do not form precipitated layers.

However, it is known that the corrosion of Al_2O_3-ZrO_2-C (AZC) slide gate plates increases when they are used for the casting of Ca-added steel [1]. Figure 4 shows the diameter change of AZC slide gate plates used for Ca-added steel casting at Kimitsu steel works of NSSMC. The diameter of the slide gate plate hole increased as the number of heats increased. This phenomenon is much sharper in the case of Ca-added steel casting.

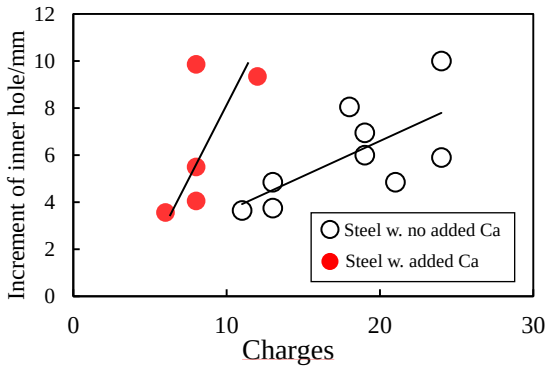

Fig.4: The diameter change of AZC slide gate plates used for casting steel with and without added-Ca at Kimitsu steel works of NSSMC

Low-melting calcium-aluminate inclusions are formed when the added-Ca reacts with the Al_2O_3 aggregate in the refractories. According to the Al_2O_3-CaO phase diagram, the eutectic point of this calcium aluminate material is 1713K (1440°C). So a liquid phase is formed on the working surface of the slide gate plates. It is said that the removal of the low-melting point layer by the molten steel stream is the main wear mechanism of the AZC slide gate plates by Ca-added steel [2]. Several trials such as the densification of the refractory materials by the control of the particle sizing [3], and the optimization of the chemical content of the Al_2O_3-ZrO_2 aggregate [4] to avoid the formation of low-melting point material have been examined. But the refractory which has sufficient corrosion resistance against Ca-added steel has not yet been developed. So the purpose of this research was to develop a high corrosion resistant material for slide gate plates.

MICROSCOPIC ANALYSIS

To achieve the purpose, used AZC slide gate plates were evaluated by microscopic analysis. A sample was cut from the working surface of middle plates used for Ca-added steel. The sample was analyzed by EPMA (Electron Probe Micro Analyzer) (JXA-810, JEOL).

Figure 5 shows the structure of a slide gate plate before and after use. It became clear that there were many more pores in the used AZC plates, than in the unused plates.

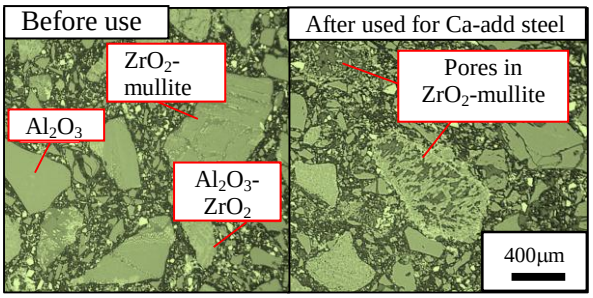

Fig.5: Structure of AZC slide gate plates
(left: before use, right: after use for Ca-added steel)

Figure 6 shows the Si and Ca maps before and after use, as obtained by EPMA. It was clear that the Si which was detected before use disappeared after use for Ca-added steel casting, and many pores developed. Furthermore, calcium aluminates penetrated into the slide gate plate structure, along the pores. It was considered that the corrosion of the AZC slide gate plates was accelerated by the pores that developed in the structure during use.

Therefore, the reason why Si disappeared preferentially from the ZrO_2-mullite aggregates was examined by thermodynamic calculation.

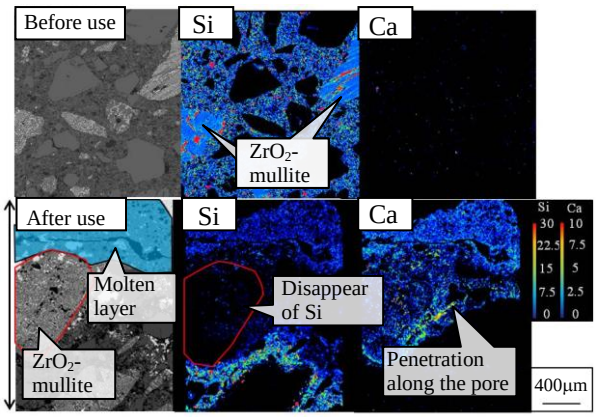

Fig.6: Si and Ca maps by EPMA

THERMODYNAMIC CALCULATIONS

Thermodynamic calculations were conducted for the condition where solid state Al_2O_3, ZrO_2, mullite and C, which are components of the refractory materials, coexisted with pure Fe or Fe-Ca in the liquid condition at temperatures from 1673K (1400 °C) to 1823K (1550 °C). Table 1 shows the conditions for the thermodynamic calculations. We assumed the coexisting species as shown in Table 1.

Tab. 1: Conditions of thermodynamic calculations

Case	Solid phases	Liquid phases	annotation
1	Al_2O_3,ZrO_2 SiO_2,C	Fe	Normal steel
2	Al_2O_3,ZrO_2 SiO_2,C	Fe-Ca, Al_2O_3-CaO	Ca-added steel Ca:20ppm, a_{CaO}=0.01

The chemical equations for the main species when the slide gate plate coexists with normal steel are shown below:

$C(s) + 1/2O_2(g) = CO\ (g)$ eq.1
$C(s) + O_2(g) = CO_2\ (g)$ eq.2
$ZrO_2(s) = ZrO(g) + 1/2O_2(g)$ eq.3
$SiO_2(s) = SiO(g) + 1/2O_2(g)$ eq.4
$Al_2O_3(s) = Al_2O(g) + O_2(g)$ eq.5
$1/2Al_2O_3(s) = AlO(g) + 1/4O_2(g)$ eq.6
$C(s) = C(g)$ eq.7
$ZrO_2(s) = ZrO_2(g)$ eq.8
$SiO_2(s) = SiO_2(g)$ eq.9
$Al_2O_3(s) = Al_2O_3(g)$ eq.10

From the Gibbs energy of formation [5], the equilibrium partial pressure of the gas species was calculated for each temperature considered. For example, focusing on the oxidization reaction of C, shown as eq.1, the equilibrium partial pressure of CO can be described as follows:

$$p_{CO} = K_{CO} \cdot a_C \cdot p_{O_2}^{1/2} \qquad \text{eq.11}$$

where K_{CO} denotes the equilibrium constant of eq.1, and a_c denotes the activity of C in this system, and p_i denotes the partial pressure of component i. The partial pressure of the other gases can also be described in a similar manner. For the assumption that the total pressure is 1 atm., the following equation is established:

$$\sum p_i = 1 \qquad \text{eq.12}$$

The equilibrium partial pressure of each component was calculated from eq.12, for each temperature considered.

On the other hand, when the slide gate plate coexisted with Ca-added steel, the following chemical equation was added.

$Ca + 1/2\ O_2\ (g) = CaO\ (l)$ eq.13

The equilibrium partial pressure of the gas species was calculated for each temperature in a similar way. Figure 7 shows the equilibrium partial pressures of the main slide gate plate components. It became clear that the partial pressure of SiO and ZrO in the case of Ca-added steel was about 100 times higher at 1823K (1550 ºC) than the partial pressure for the case of steel with no added Ca. On the other hand, with Ca in the steel, the partial pressure of oxygen became lower. This indicated that the aggregate would easily gasify when coexisting with Ca. Especially, because the partial pressure of SiO gas was extremely high, many more pores would be developed than the original material, when these slide gate plates were used for casting Ca-added steel.

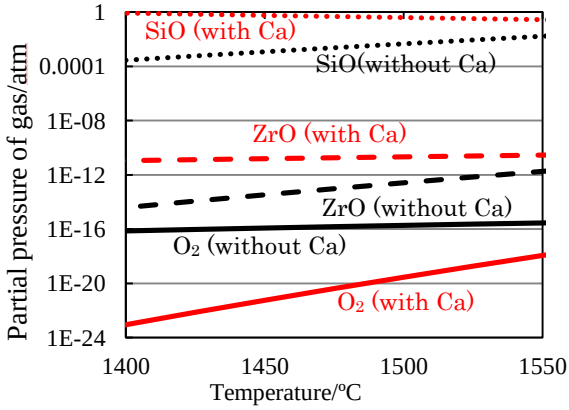

Fig.7: Equilibrium partial pressure of the main components in the slide gate plate material

INCREASING THE CORROSION RESISTANCE

Based on the thermodynamic calculations, it was determined that improving the slide gate corrosion resistance against Ca, would require development or selection of an oxide aggregate that was more stable than the ZrO_2-mullite aggregate. Aggregates which contain CaO would be very stable and therefore were eligible to be replacement aggregates for ZrO_2-mullite aggregate. However, many kinds of aggregate which contain CaO, i.e. dolomite (CaO-MgO), have a problem of slaking/hydration.

But, calcium hexaluminate (CA6) does not have the problem of slaking, and has very little tendency to gasify at high temperature. So CA6 was considered as the candidate aggregate to replace ZrO_2-mullite. Therefore, experimental refractory samples containing CA6 aggregate, for suppressing the SiO gas generation, were prepared. This model slide gate plate material, in which CA6 and Al_2O_3 were substituted for ZrO_2-mullite aggregate, is now used at Kimitsu Works of NSSMC. The test mixes had substitution of 5 and 10 wt.% CA6. Table 2 shows the composition of the initial base material and the two test mixes. The corrosion resistance of the sample materials against Ca-added steel and the thermal spalling resistance were tested.

Tab. 2: Chemical composition of base material and sample materials

material	Base	Sample1	Sample2
Al_2O_3	76	87	85
ZrO_2	13	-	-
CaO	-	2	4
F.C.	5	5	5
CA6 content	-	5 wt.%	10 wt.%

EXPERIMENTAL PROCEDURE

For the corrosion test, samples of 20 mm outside diameter and 120 mm length were prepared. The samples shown in Table 2 were dipped into 5 kg of molten steel having the same chemical composition of the Ca-added steel shown in Table 3 at 1873K (1550 ºC) for 1 hr. Because Ca in steel is very easily oxidized, and removed from steel, the test apparatus was kept under an Ar atmosphere to minimize the removal of Ca by oxidization. The corrosion resistance of the samples was evaluated by the sample size reduction. Figure 8 shows a schematic view of the corrosion test setup.

Tab. 3: Composition of the steel used for the corrosion test (unit: wt.%)

C	Si	Mn	P	S	Ca
0.43	0.09	0.58	0.01	0.0096	0.0021

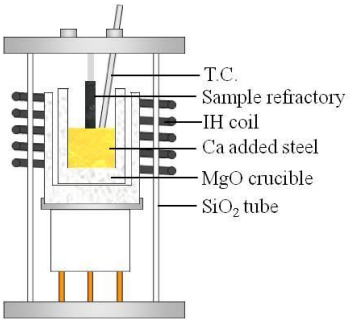

Fig.8: Schematic view of corrosion test setup

The thermal spalling resistance was evaluated by the dipping method. Samples that were 40 mm square and 160 mm long were prepared. The samples were dipped into molten pig iron for 10 min. and withdrawn from the pig iron, followed by natural cooling for five minutes. The heating and cooling cycles were repeated five times. The effect of the thermal cycling spalling was evaluated by the reduction in Young's modulus. Less reduction in Young's modulus indicated that the thermal spalling resistance of the material was better.

RESULT AND DISCUSSION

Figure 9 shows the corrosion ratio of the samples. It was revealed that the corrosion resistance of the sample materials in molten Ca-added steel, was 30 % better than the conventional (base) AZC slide gate material.

Figure 10 shows the EPMA maps of Al and Ca for the base material and sample 1. A CaO-Al_2O_3 liquid layer, which was generated from the reaction between the CaO contained in the steel and Al_2O_3 aggregate in the refractory, can be seen in both materials. But the thickness of the CaO-Al2O3 liquid layer on the base material is much thicker than the sample material containing 5 wt.% of CA6 aggregate. Ca penetrated into the matrix of the base material. On the other hand, Ca penetration into the developed sample did not occur because CA6 suppressed the gas generation from the material, and maintained the dense structure.

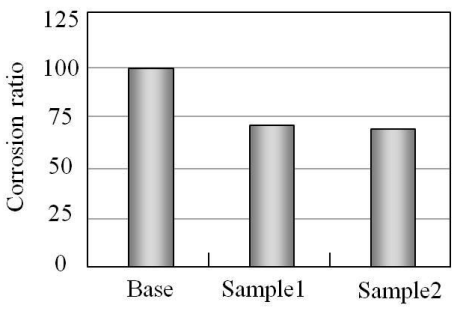

Fig.9: Results of the corrosion test

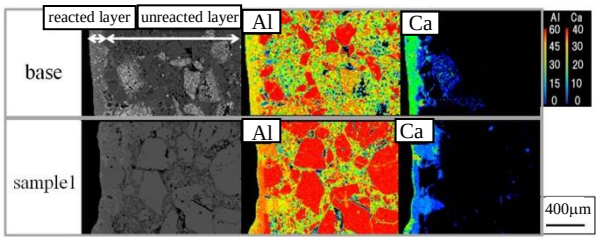

Fig.10: Al and Ca maps of samples after corrosion test

Table 4 shows the result of the spalling test. The reduction of Young's modulus of the base material was slightly more than samples 1 and 2. So the thermal spalling resistance of the developed samples was observed to be better than the base material.

Tab. 4: Result of spalling test

Material	Young's Modulus [GPa]		Reduction ratio
	before	After	
base	77	24	69%
sample1	85	30	65%
sample2	87	33	61%

So this study revealed that the developed material, containing CA6, had higher corrosion resistance to Ca-added steel, and maintained high thermal spalling resistance.

CONCLUSIONS

Based on the microscopic evaluation of used AZC slide gate plates, it became clear that when these slide gate plates were used for casting Ca-added steel, many more pores were developed in the structure than the original material, and calcium aluminates penetrated into the slide gate plate structure along the pores. It was considered that because more pores developed in the structure, the corrosion of the AZC slide gate plates was accelerated.

The mechanism of gas generation from the refractory materials was investigated by thermodynamic calculations. The analysis indicated that the partial pressure of SiO gas generated in the slide gate plate material, when used with Ca-added steel, was much higher than for other steels. So the sample refractory material, to which CA6 aggregate was added, aiming to suppress the SiO gas generation, because of its stability in the solid state, was tested for corrosion by Ca-added steel at 1823K (1550 ℃). It was determined that the corrosion resistance of the sample material was 30% better than the conventional AZC slide gate material.

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