

# Development of Metal Chromium-added Alumina-carbon Slide Valve Plates

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## Abstract

Al<sub>2</sub>O<sub>3</sub>-C containing metal Al is widely used for the slide valve plates in the continuous casting of steel. However, this material has some aspects that need to be further improved. For example, it sometimes lacks corrosion resistance in the case of casting Ca-treated steel.

In this research, we developed metal chromium (Cr)-added Al<sub>2</sub>O<sub>3</sub>-C, as a new material for the plates. Ladle plates made of this material were trialed in a steel mill for the casting of Ca-treated steel and ordinary steel. They showed less damage and longer service life than the conventional material plates. This is considered to be because Cr played roles in hindering the reduction reaction of fine Al<sub>2</sub>O<sub>3</sub> grains by carbon in the material matrix and inhibiting the penetration of molten steel and slag due to Cr increasing the viscosity of molten steel and slag.

By basic investigation, it was found that Cr carbides and nitrides were formed in the new material during the firing and this material showed smaller microstructural deterioration after reaction with molten steel and smaller corrosion after reaction with molten slag than the conventional material.

## 1. Introduction

Alumina carbon (Al<sub>2</sub>O<sub>3</sub>-C) is widely used as a material for slide valve plates for the continuous casting of steel. It generally contains metal aluminum (Al), because Al has a high reactivity with oxygen from low temperature and the final reaction product has a high melting point and thus strengthens the plate strength and improves the oxidation resistance and corrosion resistance.

However, this material has some aspects that need to be further improved<sup>1-3)</sup>. For example, it sometimes lacks corrosion resistance in the case of casting Ca-treated steel, and after being heated, its elastic modulus becomes higher, leading to a decrease in the thermal shock resistance. Moreover, aluminum carbide is formed, which may make the plates hydrated.

As an improvement measure, adding metal silicon has been known. However, the final reaction product SiO<sub>2</sub> reduces the plate corrosion resistance, so the amount of silicon additive must be limited.

We thought that reducing the Al addition should also be a way to improve it. We decided to maintain an Al

minimum addition amount to retain the advantages of Al addition at the same time.

Meanwhile, we investigated the effects of metal chromium (Cr) addition. Finally, Cr-added material for the plates was developed. Choosing metal Cr was based on the consideration that both Cr and its oxide have high melting points, beneficial to improving the plate corrosion resistance, and Cr may produce compound carbides with aluminum carbide and thus improve the plate hydration resistance.

In this report, we show the results of both basic investigation on the Cr-added material (new material) and practical trials of ladle plates made of the new material, and discuss the roles of Cr in the new material.

## 2. Basic Investigation

### 2. 1 Experimental method

Specimens of the conventional and new materials were made according to the plate production process, "mixing → forming → firing". The main component of the firing atmosphere was nitrogen. The microstructures of the fired specimens were measured by EPMA analysis.

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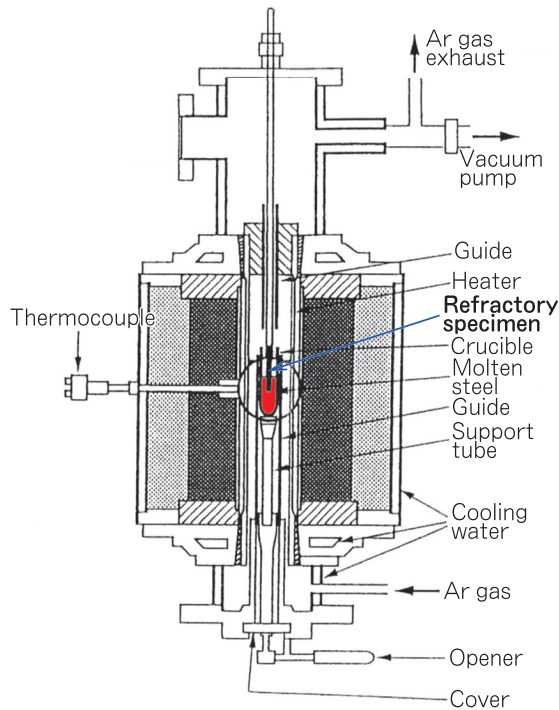


Fig. 1 Schematic diagram of tamman furnace used for investigation of reaction between molten steel and refractories.

The surfaces of the samples for EPMA analysis were precisely ground and coated with carbon beforehand (other EPMA analyses described later were the same).

Next, a molten steel reaction experiment was carried out to examine the microstructural change (deterioration) of the materials due to the reaction. A longitudinal tamman furnace shown schematically in Fig. 1 was used in this experiment. 300 grams of Ca-treated steel in an alumina crucible was heated and held at 1560 °C in an argon atmosphere. Then, the material specimen with 6 × 6 mm width was immersed into the molten steel for 30 minutes.

Molten slag reaction experiment was also conducted to investigate the corrosion resistance against molten slag. A square crucible composed of the material specimens with CaO-Al<sub>2</sub>O<sub>3</sub> system slag, as shown in Fig. 2, was heated at 1560 °C for 60 minutes in an argon atmosphere. The inside dimensions of the crucible were 20 × 20 mm, and the slag weighed 25 grams.

EPMA analyses were performed for the specimens after the molten steel reaction experiments and slag reaction experiments.

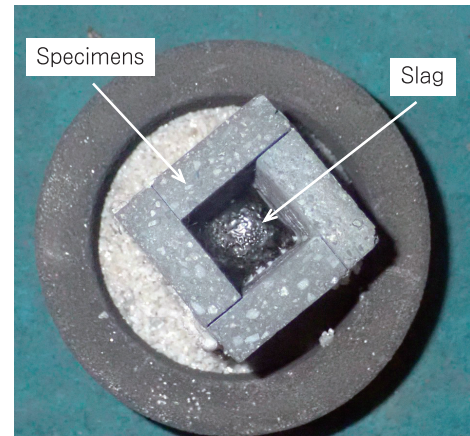


Fig. 2 Crucible composed of specimens and slag used in molten slag reaction experiment.

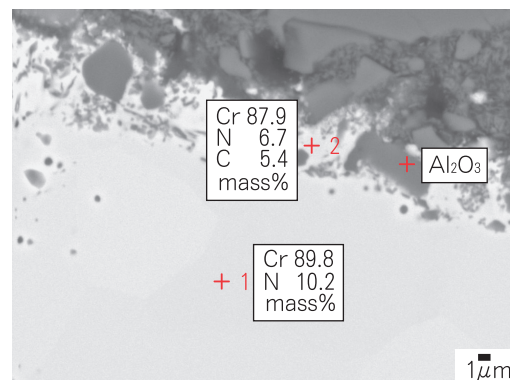


Fig. 3 EPMA analysis of Cr grains in fired specimen of new material.

## 2. 2 Results

The results of EPMA analysis for the fired new materials are shown in Fig. 3. The Cr grains were found to have decomposed and moved between the surrounding aggregate grains such as Al<sub>2</sub>O<sub>3</sub>, where the original pores were filled with Cr.

Nitrogen (N) up to about 10 mass% (hereinafter referred to as %) was detected in the Cr grains (Point 1). In the edge of the Cr grains (Point 2), carbon was also detected, where the carbon content was estimated by subtracting the analytical value of the coating carbon on the surface.

As shown in Fig. 4, Al-Cr alloy grains such as Al-Cr-C (Point 1) and Al-Cr-N (Point 2) also existed.

The above-mentioned results indicate that the nitrogen in the atmosphere entered the Cr grains and Cr carbides and nitrides were in-situ formed during the firing.

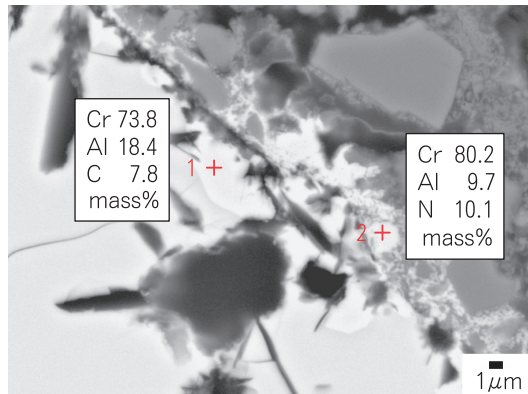


Fig. 4 EPMA analysis of Al-Cr alloy grains in fired specimen of new material.

Fig.5 shows the appearance and EPMA analysis results of the conventional and new material specimens after the molten steel reaction experiment. No damage was observed from the appearance of both specimens, whereas there was some steel skull on the immersion parts. There was less skull on the new material than on the conventional material.

A microstructural deterioration zone was formed in the matrix of both materials. But the deterioration zone was thinner in the new material, and the deterioration degree was smaller. Its penetration depth of molten steel was

also shallower.

Almost no Ca was detected in the deterioration zone by EPMA analysis, though Ca-treated steel was employed in the experiments.

Fig. 6 shows the longitudinal section microstructure of the specimens (crucibles) after the slag reaction experiment. Corrosion occurred in both specimens, but the new material showed relatively small corrosion on the whole. The largest corrosion occurred near the slag surface for both specimens. The thickness reached around 3 mm for the conventional material, but only about 1 mm for the new material.

By EPMA analysis, it was found that both the slag in contact with the specimen surface and the penetrating slag were  $\text{Al}_2\text{O}_3$ - $\text{CaO}$ - $\text{SiO}_2$  system containing  $\text{Cr}_2\text{O}_3$  up to approximately 2 %.

The nitrogen in the Cr grains remaining in the surface side of the specimen was lower than that before the molten steel or slag reaction experiments, or completely disappeared. An example is shown in Fig. 7. This indicates that nitrogen was released from the Cr grains during the reaction experiments.

Moreover, as shown in Fig. 7, there were fine Cr grains below  $1 \mu\text{m}$  in the slag.

On the other hand, Fig. 8 illustrates the thermal expansion rate of the conventional and new materials after firing. The new material had no abnormal thermal expansion behavior, similar to the conventional material.

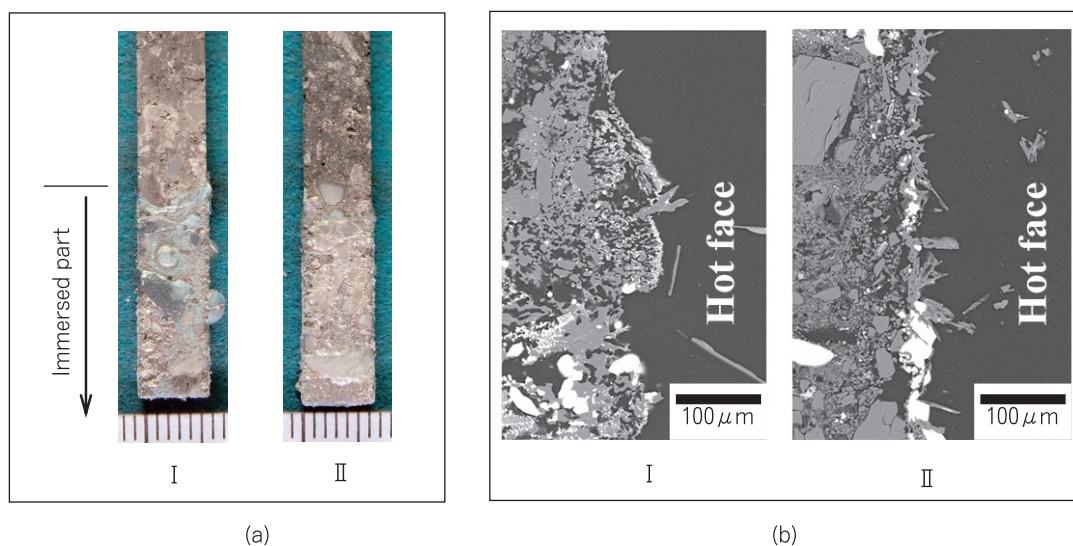


Fig. 5 Appearance (a) and hot face microstructure (b) of specimens after molten steel reaction experiment.  
(Ar,  $1560 \text{ }^\circ\text{C} \times 30 \text{ min}$ )  
I - Conventional material  
II - New material

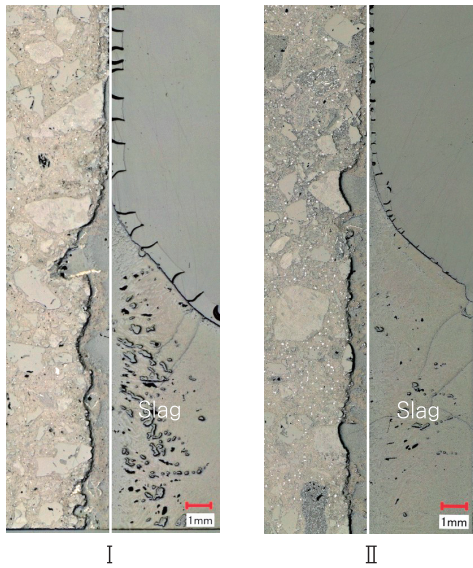


Fig. 6 Cut section of specimens (crucibles) after molten slag reaction experiment.  
(Ar, 1560 °C×60 min)  
I - Conventional material  
II - New material

The hydration resistance of the two materials was also evaluated under conditions that the pressure was 0.51 MPa, the temperature and keeping time were 154 °C and 3 hr, respectively. The weight change rate was 0.57 % for the conventional material, 0.16 % for the new material. So, the latter is believed to have higher hydration resistance.

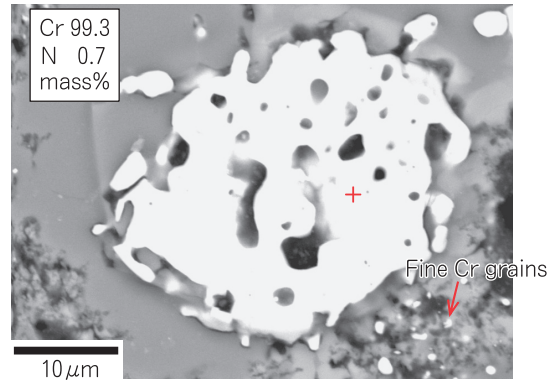
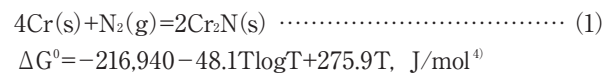


Fig. 7 EPMA analysis of Cr grains at interface between refractory (left side) and slag after slag reaction experiment.

### 2. 3 Discusses

#### 1 ) Phase changes of Cr during firing

There are two known types of Cr nitrides, namely Cr<sub>2</sub>N (N:11.9 %) and CrN (N:21.2 %). The Cr-N phase detected in the fired specimen (see Fig. 3) should be Cr<sub>2</sub>N according to its nitrogen content. That is, nitrogen (N) in the atmosphere moved into the Cr grains and reaction (1) took place during the firing.



Judging from calculation by using  $\Delta G^0$  of reaction (1), this reaction start at a low temperature under the firing conditions.

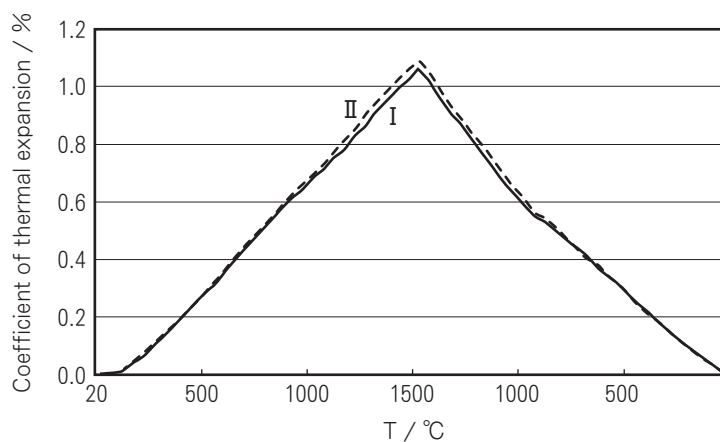


Fig. 8 Coefficient of thermal expansion of fired specimens.  
I - Conventional material  
II - New material



In addition, it is guessed that the  $\text{Cr}_2\text{N}$  in the edge of the Cr grains reacts with the surrounding carbon to form Cr-C-N phase, which was distributed between the aggregate grains. Metal Cr has a melting point as high as  $1907^\circ\text{C}$  and its equilibrium vapor pressure is low (e.g.,  $10^{-9}$  atm level at  $1000^\circ\text{C}$ ). So, the Cr movement between the aggregate grains is concluded to be not due to Cr evaporation during the firing.

Practically, a confirmation experiment was also conducted, where single metal Cr was heated in a nitrogen atmosphere. The results indicated that the weight of Cr sample increased and  $\text{Cr}_2\text{N}$  was formed, but the Cr grains did not decompose, as shown in Fig. 9.

On the other hand, it is known that there is a composite carbide,  $\text{AlCr}_2\text{C}$  (Cr:72.7, Al:18.9, C:8.4%), in Al-Cr-C system<sup>5)</sup>. The Al-Cr-C phase (see Fig. 4) in the edge of the Al-Cr grains is presumed to be  $\text{AlCr}_2\text{C}$ , since its composition was close to that of this composite carbide.

The amount of Cr carbides and nitrides can be controlled by adjusting the factors such as the grain size of raw materials, firing temperature and firing time.

## 2) Roles of Cr

It is considered that the damage of plate sliding surface is strongly related to the microstructural deterioration, which is caused mainly by the reduction (e.g., reaction (2)) of  $\text{Al}_2\text{O}_3$  fine grains by carbon in the matrix near the material surface and the dissolution of the generated gases into molten steel<sup>6)</sup>.



Compared with carbon, especially carbon black, the reactivity of Cr carbides and nitrides with  $\text{Al}_2\text{O}_3$  is much lower. So, the reduction such as reaction (2) is hindered

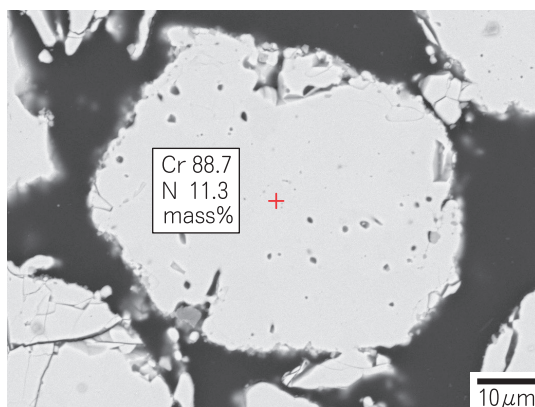


Fig. 9 EPMA analysis of single Cr grains heated in nitrogen atmosphere.

because of the formation of Cr carbides and nitrides around  $\text{Al}_2\text{O}_3$  grains. This is probably the main reason why the new material had less microstructural deterioration after the molten steel reaction experiment.

The degraded microstructure is porous, so molten steel is easy to penetrate into it. Therefore, the smaller the deterioration degree, the lower the tendency of molten steel penetration.

The penetration is also related to the viscosity of molten steel. It is generally known that, in the usual compositions of steel, Al significantly reduces the viscosity of molten steel, whereas Cr significantly increase the viscosity<sup>7)</sup>. The Cr in the new material is considered to dissolve partially into the penetrating steel (steel skull) and thus increase the viscosity, which also slows down the molten steel penetration.

On the corrosion by molten slag, Cr and its carbides and nitrides are believed to be practically insoluble in slag. The corrosion of the materials should be mainly caused by the  $\text{Al}_2\text{O}_3$  aggregate dissolving into the molten slag bulk and the penetrating slag.

It is inferred that the Cr-containing phases were oxidized by slag and thus a small amount of  $\text{Cr}_2\text{O}_3$  was formed, which dissolved into the slag and then raised the slag viscosity.

On the other hand, it has been reported that a certain amount of nitrogen (N) can dissolve in molten slag and greatly increase the slag viscosity, slowing down the slag penetration into refractories<sup>8)</sup>. In the case of the new materials, nitrogen (N) released from the Cr nitrides (the inverse reaction of reaction (1)) at high temperature may have dissolved in the slag and increased its viscosity.

Moreover, the slag viscosity should be raised also due to the presence of the fine Cr grains (see Fig. 7).

Because the slag viscosity increased, the dissolution of the aggregates in the new material became slower and so it showed higher corrosion resistance.

## 3. Practical Trials

According to the basic investigation results, slide valve plates for the ladle were made using the new material and trialed in a steel mill. The cast steel grades included Ca-treated steel and ordinary steel (ultra low carbon, low carbon and medium carbon steel). The ladle had a capacity of approximately 300 tons of steel.

75 sets of the new material plates were trialed. No troubles occurred. Fig. 10 shows the appearances of the conventional and new material plates after use, respectively. The conventional material plate was only used in the cast of the ordinary steel, while using the new

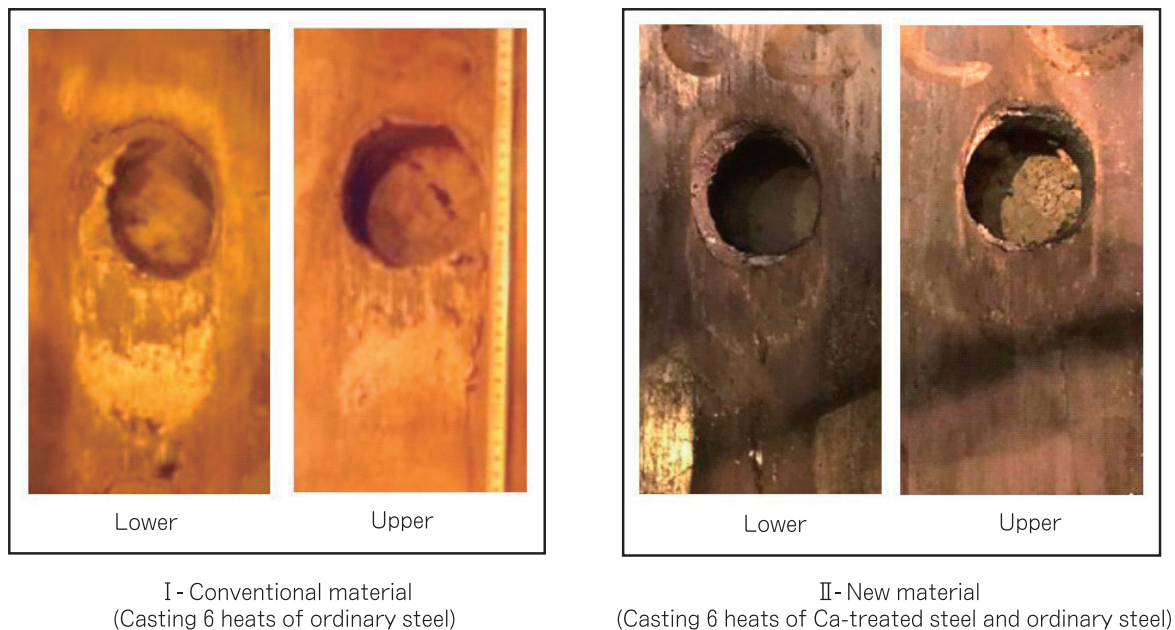


Fig. 10 Appearance of used slide valve plates.

material plate, Ca-treated steel was also cast besides ordinary steel. Even in this case, the sliding surface of the new material plate showed less damage. So, they had longer service life than the conventional material plates.

#### 4. Conclusions

Metal Cr-added  $\text{Al}_2\text{O}_3\text{-C}$  was developed as a new material for sliding valve plate for the continuous casting of steel. The basic investigation results indicated that Cr carbides and nitrides were formed in the new material during the firing. And this material showed smaller microstructural deterioration after reaction with molten steel and smaller corrosion after reaction with molten slag than the conventional material. Moreover, it had

higher hydration resistance.

Ladle plates made of this new material were trialed in a steel mill for the casting of Ca-treated steel and ordinary steel. They showed less damage and longer service life than the conventional material plates.

This is considered to be because Cr played roles in hindering the reduction reaction of fine  $\text{Al}_2\text{O}_3$  grains by carbon in the matrix of the material and inhibiting the penetration of molten steel and slag into the material due to Cr increasing the viscosity of molten steel and slag.

We will promote trials of the new material plates in more steel mills to further confirm the effects in casting Ca-treated steel and other steel grades.

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