

SHINAGAWA TECHNICAL REPORT

金属クロム添加アルミナ-カーボン質 スライドプレートの開発

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

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品川技報

報文 REPORT

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

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要 旨

鋼の連続铸造用スライドプレートの材料として、金属Al含有 Al_2O_3 -C質が広く適用されているが、Ca処理鋼に対する耐食性が不十分であるなどの不足がある。この課題を改善する手法として金属Crを併用する Al_2O_3 -C質プレート(新規材)を開発した。この新規材は実機使用において、従来材より損傷程度が小さく、高寿命を示した。この結果はCrが微細な Al_2O_3 粒のカーボンによる還元を抑制し、溶鋼およびスラグの粘度上昇によるれんが内への浸透抑制などに作用を果たしたためと考えられる。基礎検討でも、金属Crが焼成後にCr含有の窒化物および炭化物を生成し、溶鋼による組織脆化やスラグによる溶損が低減することを確認した。

Abstract

Al_2O_3 -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_2O_3 -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_2O_3 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.

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1. 緒言

鋼の連続鋳造に用いられるスライドプレートの材料として、アルミナ-カーボン($\text{Al}_2\text{O}_3\text{-C}$)質が一般的に適用されている。プレートの強度付与、耐酸化性向上、耐食性向上を目的に、金属アルミニウム(Al)が添加されている。これは Al が酸素と低温から高い反応性を有し、また、最終生成物が高融点という特徴を持つためである。しかし、この材料は、さらなる改良が必要などがある。例えば、 Ca 処理鋼に対する耐食性が不十分である。また、受熱により高弾性率化し、耐熱衝撃性が低下し、また、炭化アルミニウムの生成により耐水和性が低下するという欠点もある¹⁻³⁾。この欠点を改善する手法として、金属 Si の添加が知られているが、 Si の最終生成物 SiO_2 は耐食性低下の要因となるため過剰な添加は避けたい。 Al の減量も改善の手法の1つであるが、せっかくの Al 添加の利点が小さくなるので、 Al の利点を維持するため、最低限の添加量は維持したい。

そこで著者らは新たな改善手法として、金属 Cr 添加の検討を行った。金属 Cr を選定した理由は、その金属と酸化物ともに高融点であることから耐食性向上が期待でき、また、単体炭化アルミニウムの生成を抑制する炭化クロムを生成することから耐水和性向上にもつながる可能性があると考えられたためである。本報告では、その基礎検討および実機テストの結果を示し、 Cr 作用のメカニズムを考察した。

2 基礎検討

2. 1 実験方法

「混練→成形→焼成」のプレート製造プロセスにて従来材料(従来材)および金属 Cr 添加材料(新規材)の試料を作製した。焼成雰囲気は、窒素ガスを主組成とした。焼成後試料については、まずEPMA分析で微組織を調査した。EPMA分析では、サンプルを精密に研磨し、表面にカーボンを蒸着した(後述するその他のEPMA分析でも同様)。

次に、溶鋼との反応による試料の組織変化(脆

1. Introduction

Alumina carbon ($\text{Al}_2\text{O}_3\text{-C}$) 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 improved¹⁻³⁾. 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_2 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

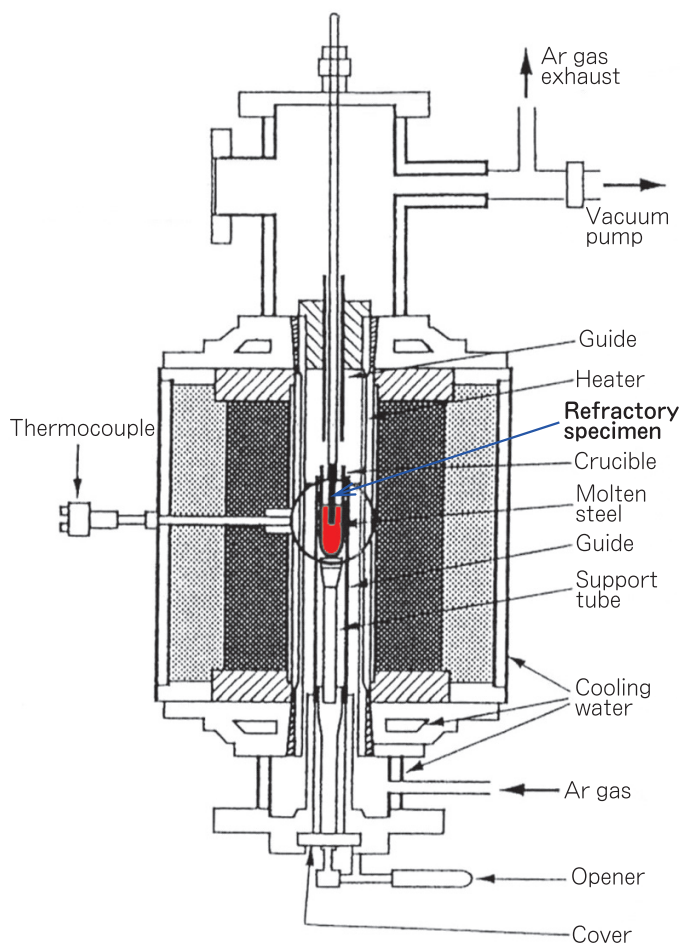


Fig. 1 Schematic diagram of tamman furnace used for investigation of reaction between molten steel and refractories.

化)を調べた。この場合、縦型タンマン炉(Fig.1)を用いた。アルゴン雰囲気中で、アルミナルツボに300gの低炭Ca処理鋼を溶解し、1560℃に保持後、幅6×6mmの試料を30min浸漬した。

また、溶融スラグとの反応による溶損状況を調べた。板状の試料で組み立てた正方形のルツボ(内側20×20mm)にCaO-Al₂O₃系スラグ(25g)を入れ(Fig.2),「アルゴン雰囲気, 1560℃×60min」の条件で加熱した。

以上の溶鋼反応およびスラグ反応実験後試料について、EPMA分析を行った。

2.2 結果

焼成後新規材試料のEPMA分析結果をFig.3に示す。Cr粒は分解し、その周囲のAl₂O₃など骨材粒間へ移動した。その粒間にあった気孔は、Crに

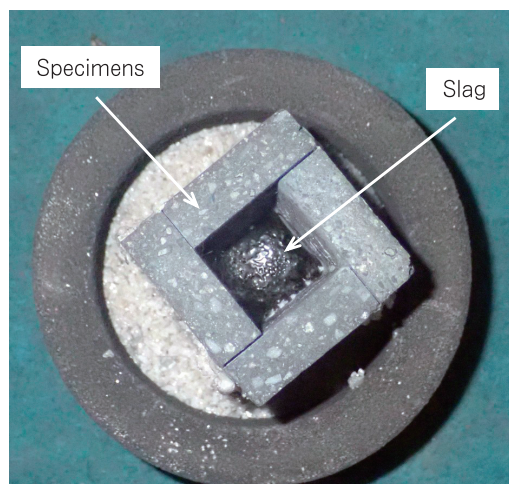


Fig. 2 Crucible composed of specimens and slag used in molten slag reaction experiment.

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. 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-Al₂O₃ 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

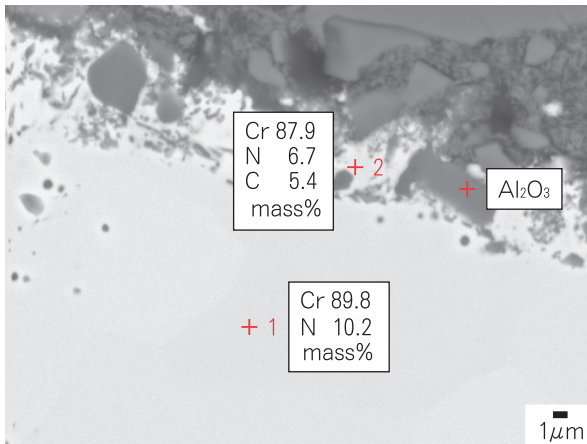


Fig. 3 EPMA analysis of Cr grains in fired specimen of new material.

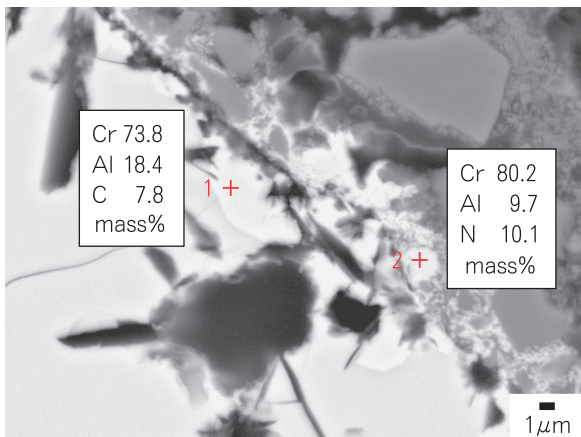


Fig. 4 EPMA analysis of Al-Cr alloy grains in fired specimen of new material.

よって充填された。また、Cr粒には約10mass%（以下、mass%を%と略する）と多量の窒素(N)が検出された(Point 1)。なお、Cr粒の外周側にはカーボン(Point 2)も認められた（サンプル表面の分析用蒸着材であるカーボンの分を除いた推算）。なお、Fig.4に示すように、Al-Cr-C(Point 1)およびAl-Cr-N系(Point 2)の相からなるAl-Cr系合金の粒も存在している。これらより、焼成中に雰囲気中の窒素がCrに入り、その場生成相であるCrの炭化物および窒化物が生じていることが判明した。

specimens after the molten steel reaction experiments and slag reaction experiments.

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 Al₂O₃, where the original pores were filled with Cr.

Nitrogen (N) up to about 10 mass% (herein-after 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.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

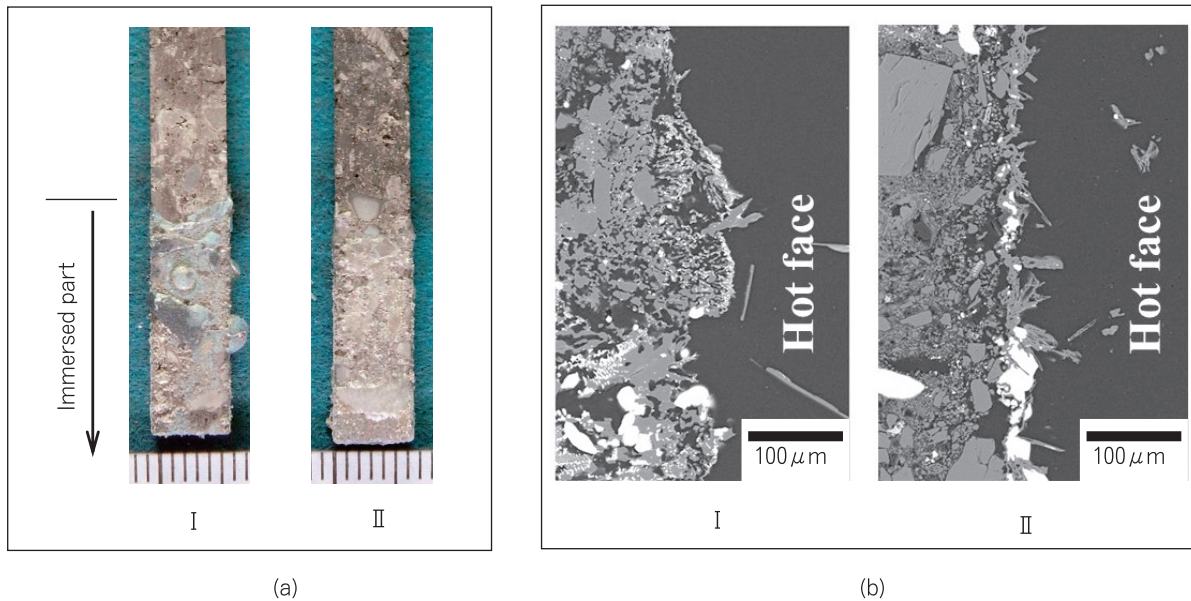


Fig. 5 Appearance (a) and hot face microstructure (b) of specimens after molten steel reaction experiment.
(Ar, 1560 °C×30 min)
I - Conventional material
II - New material

Fig.5に溶鋼反応実験後の試料の外観写真および表面側のEPMA分析結果を示す。外観上は、両試料とも溶損が生じず、表面に地金が付着していたが、新規材の方が地金付着量が少なかった。微組織では、両試料ともマトリックス部に脆化層が生じていたが、新規材の方が脆化層の厚みが薄く、脆化程度が小さい傾向が認められた。溶鋼の浸透深さも小さかった。ただし、本実験にCa処理鋼を用いたが、EPMA分析で脆化層からCa成分はほとんど検出されなかった。

Fig.6に、溶融スラグ反応実験後の試料(ルツボ)の縦方向切断面の組織を示す。両試料とも溶損が生じていたが、溶損厚みは、全体的には新規材の方が小さかった。例えば、溶融スラグ浴面付近で試料の溶損厚みが最も大きかったが、従来材の最大溶損厚みが3 mm位であったが、新規材のそれはわずか1 mm位であった。新規材試料の表面と接触しているスラグおよび内部へ浸透しているスラグは、EPMA分析により、 Cr_2O_3 を約2 %まで含む Al_2O_3 - CaO - SiO_2 系であった。

また、溶鋼反応実験後と溶融スラグ反応実験後

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 Al_2O_3 - CaO - SiO_2 system containing Cr_2O_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 μm 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.

The hydration resistance of the two materials was also evaluated under conditions that the pressure was 0.51 MPa, the temperature and

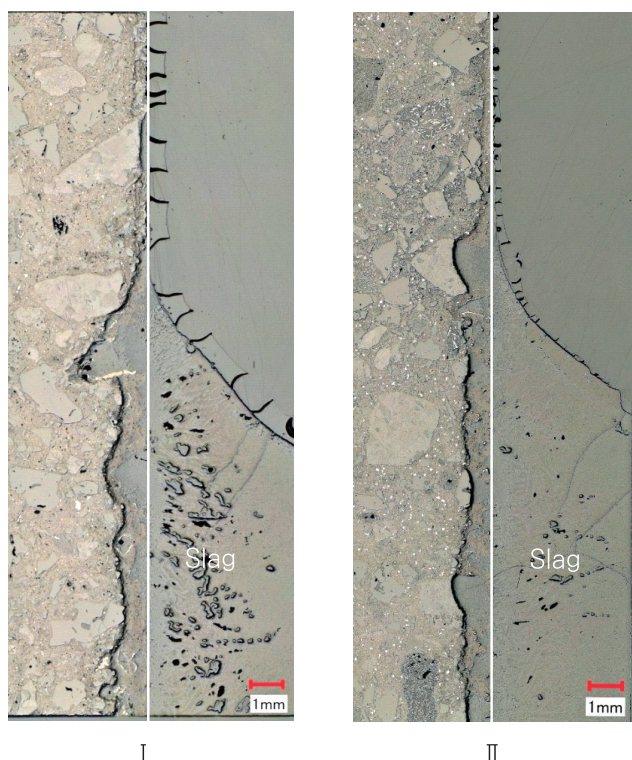


Fig. 6 Cut section of specimens (crucibles) after molten slag reaction experiment.
(Ar, 1560 °C×60 min)
I - Conventional material
II - New material

とも、試料の表面側に残存しているCr粒の窒素は実験前より低下し、またはほぼ消失した。その一例をFig.7に示す。したがって、溶鋼、溶融スラグとの反応中に、Crから窒素を放出したことがわかる。なお、Fig.7に示すように、スラグ中に1 μ m以下の微細なCr粒が存在していた。

他方、焼成後の従来材と新規材の熱膨張率をFig.8に示す。異常な熱膨張挙動は認められなかった。

また、耐水和性も評価した（圧力0.51MPa, 154°C×3hr）。テスト前後の重量変化率は、従来材が0.57%, 新規材が0.16%であり、新規材の方が耐水和性に優れる結果となった。

2. 3 考察

1) 焼成中におけるCrの相変化

Cr窒化物には、Cr₂N(N:11.9%)とCrN(N:21.2%)の2タイプがあることが知られている。焼成後の試料から検出されたCr-N系の相(Fig.3)

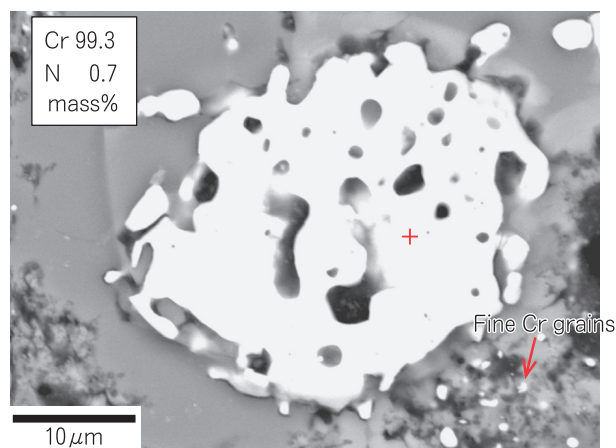


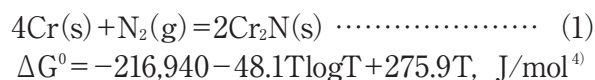
Fig. 7 EPMA analysis of Cr grains at interface between refractory (left side) and slag after slag reaction experiment.

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.

2. 3 Discusses

1) Phase changes of Cr during firing

There are two known types of Cr nitrides, namely Cr₂N (N:11.9 %) and CrN (N:21.2 %). The Cr-N phase detected in the fired specimen (see Fig. 3) should be Cr₂N 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 ΔG^0 of reaction (1), this reaction start at a low temperature under the firing conditions.

In addition, it is guessed that the Cr₂N 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 °C and its equilibrium vapor pressure is low (e.g., 10⁻⁹ atm level at 1000 °C). So, the Cr movement between

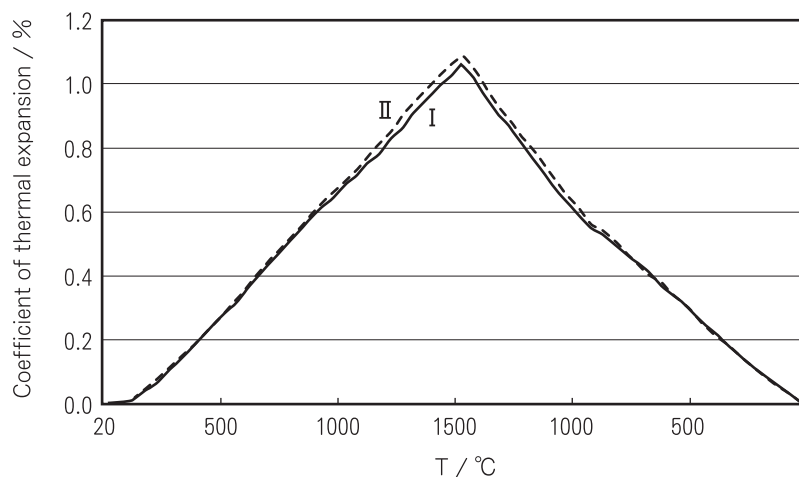
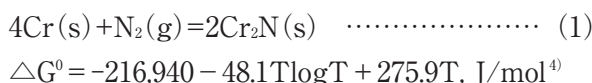


Fig. 8 Coefficient of thermal expansion of fired specimens.
I – Conventional material
II – New material

は、その窒素含有量から Cr_2N であると考えられる。すなわち、焼成中に反応(1)が起こり、雰囲気中の窒素(N)がCrへ移動した。



ΔG° を用いた計算により、本焼成条件でこの反応は低温から起こり得る。

また、Cr粒外周の Cr_2N は、その近傍のカーボンと反応し、Cr-C-N系の相を生成させながら、骨材粒間へ移動したと推定される。

金属Crは1907℃と高い融点を有し、平衡蒸気圧が低い（例えば、1000℃で 10^{-9} atmオーダー）。その粒間への移動は、焼成中でのCr蒸発によるものではないと判断される。

実際に、確認のため金属Cr単体を窒素雰囲気中で加熱する実験も行った。実験後試料の重量が増加し、 Cr_2N が生成したが、Cr粒の分解は認められなかった (Fig.9)。

一方、Al-Cr-C系には複合炭化物の AlCr_2C (Cr:72.7, Al:18.9, C:8.4%) が存在することが知られている⁵⁾。Al-Cr粒の外周側におけるAl-Cr-C系の相 (Fig.4) はその組成に近いので、 AlCr_2C であると推定される。

これらCrの窒化物および炭化物の量は、原料の

the aggregate grains is concluded to be not due to Cr evaporation during the firing.

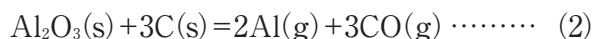
Practically, a confirmation experiment was also conducted, where single metal Cr was heated in a nitrogen atmosphere. The results indicated that the weight of Cr sample increased and Cr_2N was formed, but the Cr grains did not decompose, as shown in Fig. 9.

On the other hand, it is known that there is a composite carbide, AlCr_2C (Cr:72.7, Al:18.9, C:8.4%), in Al-Cr-C system⁵⁾. The Al-Cr-C phase (see Fig. 4) in the edge of the Al-Cr grains is presumed to be AlCr_2C , 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 Al_2O_3 fine grains by carbon in the matrix near the material surface and the dissolution of the generated gases into molten steel⁶⁾.



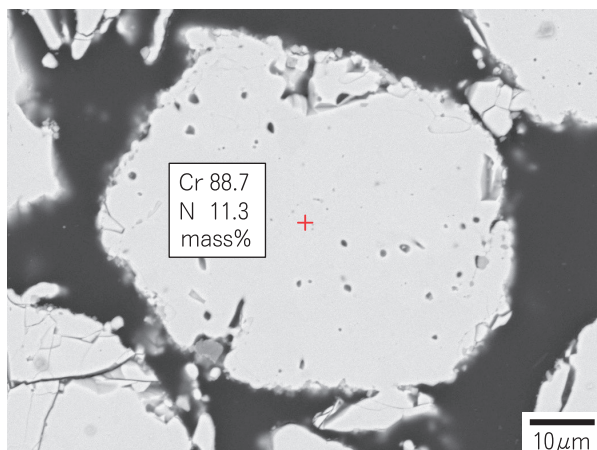
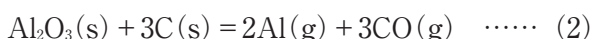


Fig. 9 EPMA analysis of single Cr grains heated in nitrogen atmosphere.

粒度，焼成温度および焼成時間などの調節によってコントロールできる。

2) Crの作用

プレート摺動面の損傷は，溶鋼との反応による組織脆化に大きく関係し，その組織脆化は，主に表面付近のマトリックスにおける微細 Al_2O_3 粒がカーボンに還元され（例えば，反応(2)），生成するガス相が溶鋼へ拡散し溶解することに起因すると言われている⁶⁾。



カーボン，特にカーボンブラックに比べて，Crの炭化物および窒化物の方が Al_2O_3 との反応性が低く，それらの Al_2O_3 粒周囲での生成によって反応(2)のような脆化を促進させる反応は進行しにくくなる。これは，新規材の方が溶鋼との反応による組織脆化が小さかった要因と考えられる。

脆化した組織はポーラス状態なので，脆化層内への溶鋼浸透の傾向が大きくなる。したがって，脆化程度が小さいほど，浸透が生じにくくなると言える。浸透は，溶鋼の粘度にもかかわる。通常の鋼中成分では，Alが溶鋼の粘度を顕著に低下させるが，Crは逆に顕著に高めることが知られている⁷⁾。新規材の場合は，浸透している溶鋼（地金）へCrの一部が溶解し，地金の粘度が高くなり，これによっても溶鋼が浸透しにくくなると考えられる。

Compared with carbon, especially carbon black, the reactivity of Cr carbides and nitrides with Al_2O_3 is much lower. So, the reduction such as reaction (2) is hindered because of the formation of Cr carbides and nitrides around Al_2O_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 viscosity⁷⁾. 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 Al_2O_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 Cr_2O_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 refractories⁸⁾. 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

一方、熔融スラグによる試料の溶損については、Crおよびその窒化物および炭化物はいずれもその熔融スラグにほとんど溶解しないと考えられる。試料の溶損は、主に Al_2O_3 骨材のスラグバルク、さらに組織内部へ浸透しているスラグへの溶解によると考えられる。

Cr系の相がスラグに酸化され、少量の Cr_2O_3 が生成し、その Cr_2O_3 溶解によってスラグの粘度が高くなると推定される。また、熔融スラグに一定の窒素(N)が溶解し、それによりスラグ粘度が顕著に高まり、スラグのれんが内部への浸透が生じにくくなるようなことも報告されている⁸⁾。新規材の場合は、高温でCr窒化物から窒素(N)を放出し(反応(1)の逆反応)、スラグに溶解することによっても、スラグの粘度が高くなると推定される。なお、スラグに存在している微細なCr粒(Fig.7)もスラグの粘度を高めると考えられる。スラグの粘度が高くなると、 Al_2O_3 骨材のスラグへの溶解が遅くなり、溶損が小さくなる。

3. 実機テスト

ラボ検討の結果から、金属Cr含有の新規材を適用した取鍋プレートを作製し、製鉄所での実機テ

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 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 Al_2O_3 -C was developed as a new material for sliding valve plate for the continuous casting of steel. The basic investigation

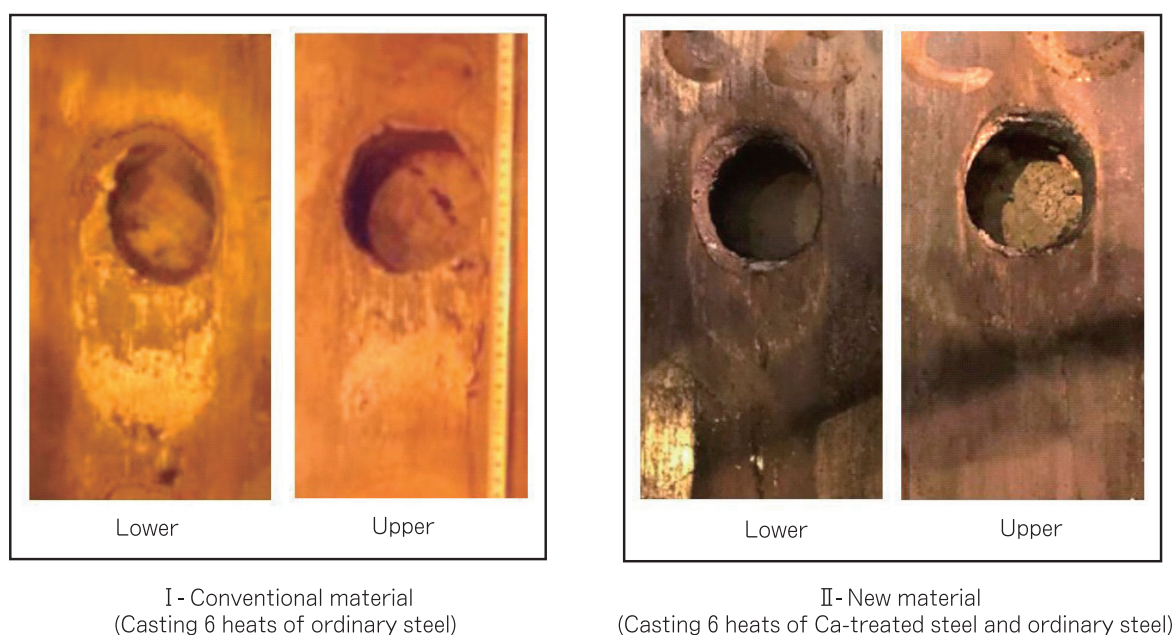


Fig. 10 Appearance of used slide valve plates.

ストに供した。鑄造した鋼種には、Ca処理鋼および普通鋼（極低炭，低炭と中炭鋼）などが含まれた。取鍋の溶鋼量は、約300tであった。

75セットテストされ、いずれも漏鋼などのトラブルは発生せず、問題なく使用された。使用後従来材と新規材プレートの外観写真をFig.10に示す。従来材が普通鋼鑄造のみに使用されたが、新規材は、普通鋼のほかCa処理鋼鑄造にも使用された。このような場合でも、新規材の方がプレート摺動面の損傷が小さかった。全体的に、新規材の方が高寿命を示した。

4. 結言

鋼の連続鑄造用スライドプレートとして、金属Crを添加した材質を検討した。その結果、金属Crは焼成によりCrの炭化物や窒化物となり、実験において溶鋼との反応による組織脆化およびスラグとの反応による溶損が小さいことを確認した。

この金属Crを併用した新規材を溶損性の高いCa処理鋼を含む実機鑄造でテストした結果、摺動面の損傷が小さく、高寿命を示した。今後、この新規材のプレートを各所へ展開し、Ca処理鋼など溶損鋼種への効果をさらに確認していく予定である。

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 Al_2O_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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