

不焼成SVプレートの開発

Development of New Unfired Slide Valve Plate Material

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Abstract

Standard materials for slide valve plates that have been manufactured by a firing process sometimes show poor performance when they are used under challenging conditions. Therefore, Shinagawa has developed a new unfired material with high aluminum content. This new material shows excellent performance and satisfies various customer requirements in Japan.

1. 緒言

スライドゲートバルブ（以下SV）は、取鍋-タンディッシュ間やタンディッシュ-モールド間の溶鋼流量制御方法として、広く普及している。

絞り注入や弱脱酸鋼鑄造などの苛酷な操業条件下で使用される取鍋用SVプレートでは、エッジ損傷と面荒れ損傷が大きくなる傾向にある。また従来から苛酷な操業条件下で使用される取鍋用SVプレートとしては一般的な焼成SVプレートが適用されていたが、上述した損傷のため高耐用化が難しい状況にあった。

そこで鑄造時の受熱に伴う添加金属の反応に着目し、熱間強度と耐食性および耐酸化性の向上を目的に、金属を多量に添加した不焼成SVプレートを開発した。実機使用の結果、従来のSVプレート材質に比べて耐用が30%向上した。

2. 開発品の特徴

絞り注入や弱脱酸鋼鑄造等の条件下にて使用される取鍋用SVプレートの主な損傷形態は、エッジ損傷と面荒れ損傷である。絞り注入では、溶鋼流

1. Introduction

The slide valve (SV) plate system is being used at many steel plants for flow control of molten steel from ladle to tundish or from tundish to mold. SV plates for ladles often showed significant damage at the bore edge and/or working surface when they had been used under arduous conditions like long hours of throttling, special grade steel casting, and so on. The performance of standard fired material for ladle SV plates under such conditions could not be improved because the above damages were often suffered. Therefore, Shinagawa developed a new unfired SV plate material with high aluminum content. This new material showed improved hot modulus of rupture, erosion resistance, and oxidation resistance by utilizing the heat reaction of aluminum that was added as aluminum powder during the mixing process. The performance was improved by 30% under actual casting conditions as a result of using the

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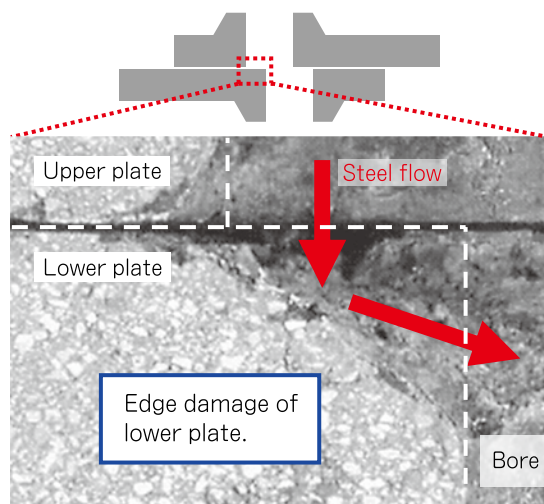


Fig. 1 Cross-section of conventional SV plate after used.

による摩耗および溶損によってエッジ損傷が拡大する (Fig. 1)。弱脱酸鋼の casting では、酸化により摺動面れんが組織が脆弱化することにより面荒れ損傷が進行する。

新材質の開発に当たり、 casting 時の受熱を利用した金属 Al からの Al_2O_3 微細組織生成に着目した結果、れんが組織を強化することにより熱間強度と耐食性および耐酸化性を向上させた新材質を開発した。通常焼成 SV プレートは、 1000°C を越える温度で還元焼成した後ピッチ含浸工程を経て製品化される。開発品では金属 Al を多量に添加するため、 500°C 以下の熱処理のみで製品化することを特徴としている (Fig. 2)。

開発品を実機使用に供した結果、エッジ損傷と面荒れ損傷が共に抑制され、比較品に比べて耐用が 30% 向上した。

new material.

2. Characteristic of Developed Material

SV plates that had been used for long hours of throttling or special steel grade casting showed damage at the bore edge and/or working surface. The bore edge damage was increased by corrosion and erosion due to steel flow while throttling as shown in Fig. 1. The working surface was damaged by oxidation and degradation of texture during special grade steel casting.

By focusing on the microstructure generated by the heat of the reaction from aluminum to Al_2O_3 , Shinagawa has developed a new SV plate material that has high hot modulus of rupture, excellent erosion resistance and greatly improved oxidation resistance. These benefits are attributable to densification of the texture of the plate. Standard SV plate materials are manufactured by firing above 1000°C in a reducing atmosphere with coke, followed by pitch impregnation. The newly developed material is manufactured by using only heat treatment under 500°C as shown in Fig. 2.

This new material shows 30% better performance compared with the conventional material. This improvement is due to a reduction in damage of the bore edge and working surface in actual use.

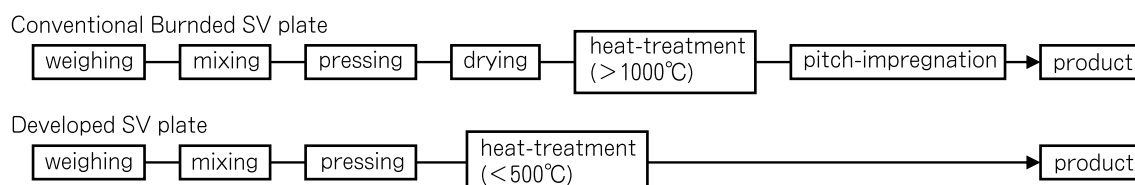
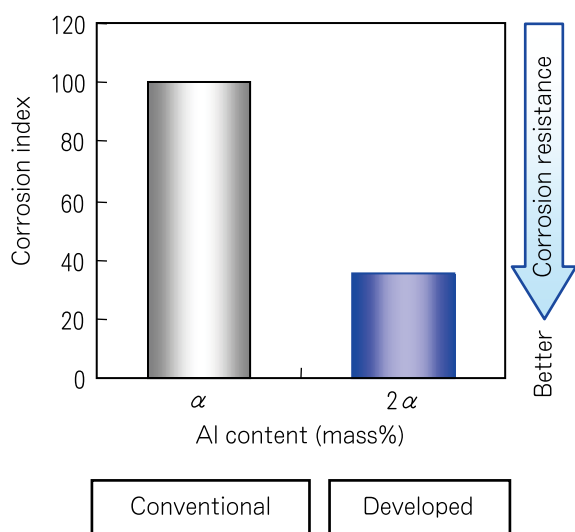


Fig. 2 Flow-chart of manufacturing process for SV plate.

Table 1 Typical properties of developed and conventional SV plate

	Conventional	Developed
Chemical composition (mass%)		
Al ₂ O ₃	82	80
SiO ₂	1	1
ZrO ₂	4	4
C	4	4
Al	α	2 α
Apparent porosity (%)	4.2	5.2
Bulk density (g/cm ³)	3.27	3.24
Cold crushing strength (MPa)	136	145
Hot modulus of rupture (MPa)	41	48

**Fig. 3** Result of corrosion test of SV plate.

3. 開発品の品質と評価試験結果

3. 1 品質特性

開発品の品質と、比較として金属Al添加量の少ない不焼成品の品質をTable 1に示す。金属Al添加量の増量添加に伴い熱間曲げ強さは高くなる。

3. 2 評価試験

開発品の耐食性をロータリースラグ侵食試験にて評価した。評価試験条件は1650℃-4時間(回転数4.5rpm)とし、普通鋼とミルスケールを1:1に調合した侵食剤300gを30分ごとに入れ替えて実施した。また試料サイズは厚さ40mm、高さ114mmとし、8角形に組んで試験を行った。試験後の侵食面積を比較した結果、開発品の耐食性は65%向上している (Fig. 3)。

開発品の耐酸化性を気相酸化試験にて評価

3. Properties and Test Results of Developed Material

3. 1 Properties

Table 1 shows the properties of the developed material and conventional unfired material having low aluminum content. The hot modulus of rupture was increased with higher content of aluminum.

3. 2 Test results

The erosion resistance of the developed material was evaluated by rotary slag test. This test was performed at 1650℃, with a 4 hour soak time at a speed of 4.5 rpm. The test slag that had been prepared using 50% standard steel and 50% mill scale was replaced every 30 minutes. Test samples were 114mm in height and 40mm thick and were assembled in an octagon shape. The resulting comparison of the eroded area after rotary slag test showed that the developed material had 65% better erosion resistance than conventional material as shown Fig. 3.

The oxidation resistance of the developed material was examined by oxidation test. This test was performed at 1200℃ with a 3 hour soak time in an electrical furnace with air atmosphere. The test samples in the form of 40 mm cubes were examined to determine the non-oxidized area and the cold crushing strength. The non-oxidized area of the developed material is 8% more than the conventional material while cold crushing strength of the developed material is 15% higher than the conventional material as shown in Fig. 4.

4. Results of Actual Casting

This new developed material was used for the ladle SV plates by customer A in Japan. Fig. 5 shows the typical damage condition (appearance and cross section) of conventional material and developed material. Fig. 6 shows the damage

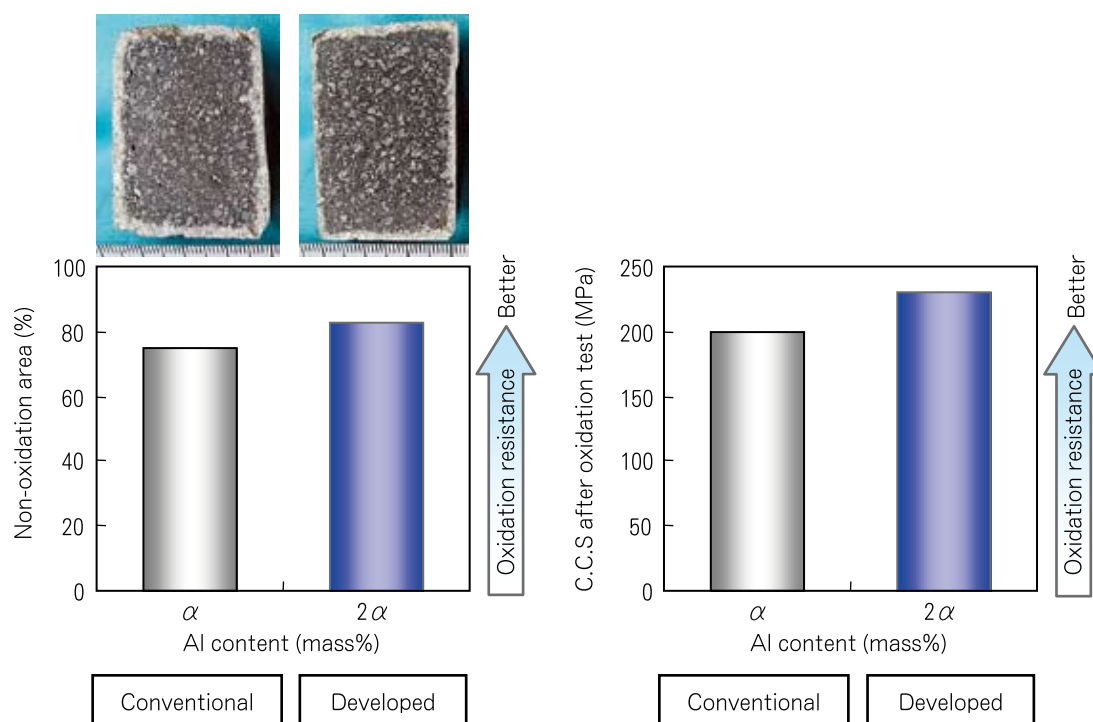


Fig. 4 Results of oxidation test of SV plate.

した。評価試験条件は40mm角の試料を1200℃ - 3時間空气中で加熱し、試験後の非酸化部面積と圧縮強さを調査した。開発品は比較品に対して残炭面積が8%多く、酸化試験後の圧縮強さも15%向上した (Fig. 4)。

4. 実機使用結果

A社取鍋にて、開発品を実使用に供した。比較品と開発品について、代表的な損傷状況の使用後品の外観および切断面をFig. 5に、エッジ損傷および面荒れ損傷速度をFig. 6に示す。比較品はエッジ損傷と面荒れ損傷のため最大6チャージまでの耐用であった。一方、開発品はエッジ損傷および面荒れ損傷が共に低減し、最大8チャージまで耐用が延び、平均使用回数は比較品が5.4チャージに対して開発品は6.9チャージと、耐用が30%向上した (Fig. 7)。

5. 使用後解析結果

5. 1 使用回数とエッジ損傷量の関係

使用途中の2チャージ、3チャージおよび

rate of the bore edge and working surface. Conventional material plates were restricted to a maximum of 6 heats by the damage of bore edge and working surface. On the other hand, the developed material plates can achieve a maximum of 8 heats due to the reduction of these damages. The average performance of the developed material at 6.9 heats was 30% better than conventional material at 5.4 heats as shown Fig. 7.

5. Analysis of the Plates after Use

5. 1 Relationship between heat number and bore edge damage

Shinagawa investigated the damage condition, physical properties and aluminum condition of the developed material plate after using for 2, 3, and 5 heats. Fig. 8 shows the relationship between heat number and bore edge damage of developed lower plate. Fig. 9 shows the relationship between heat number and rate of bore

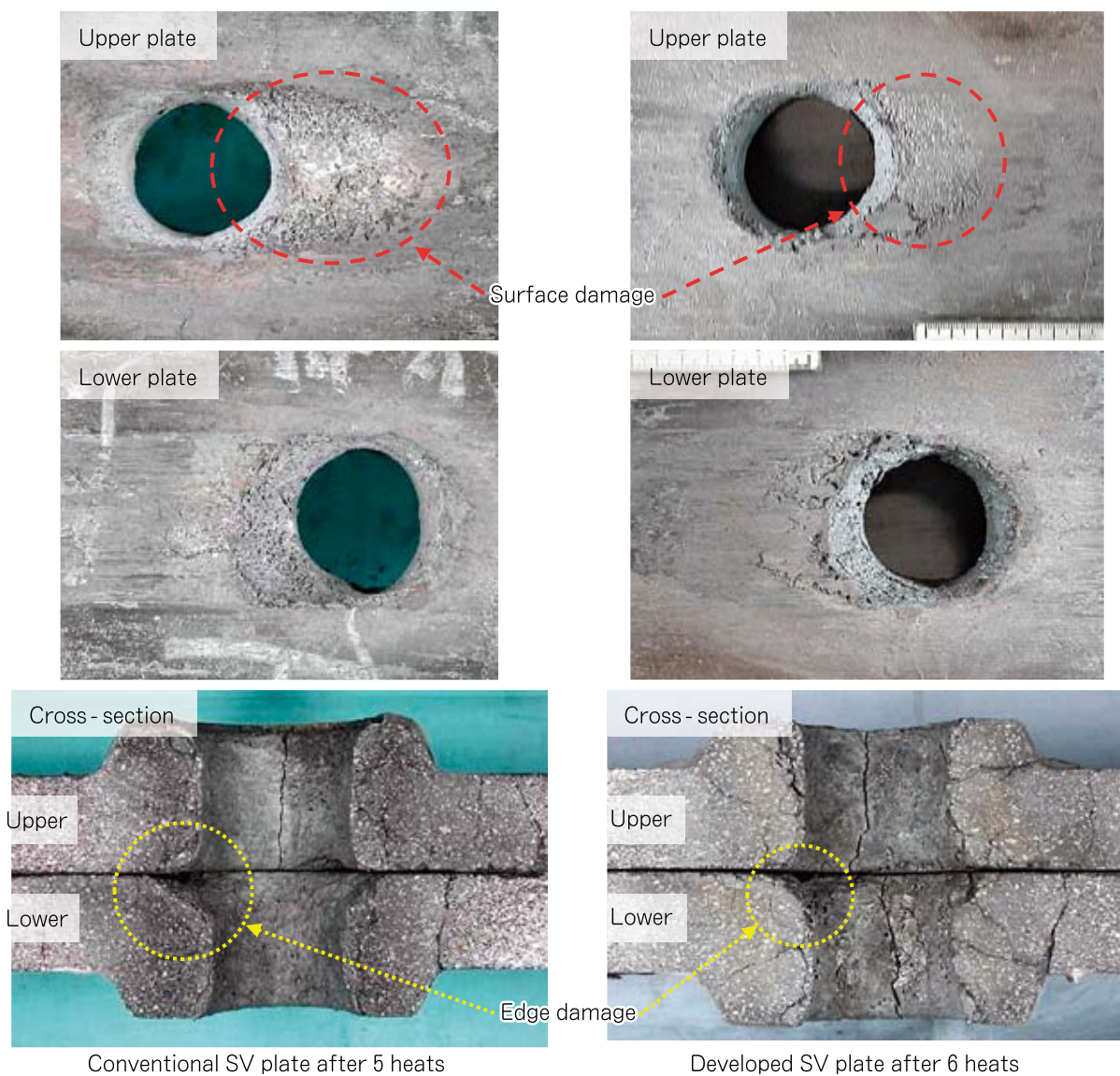


Fig. 5 Damage around bore of SV plate after used.

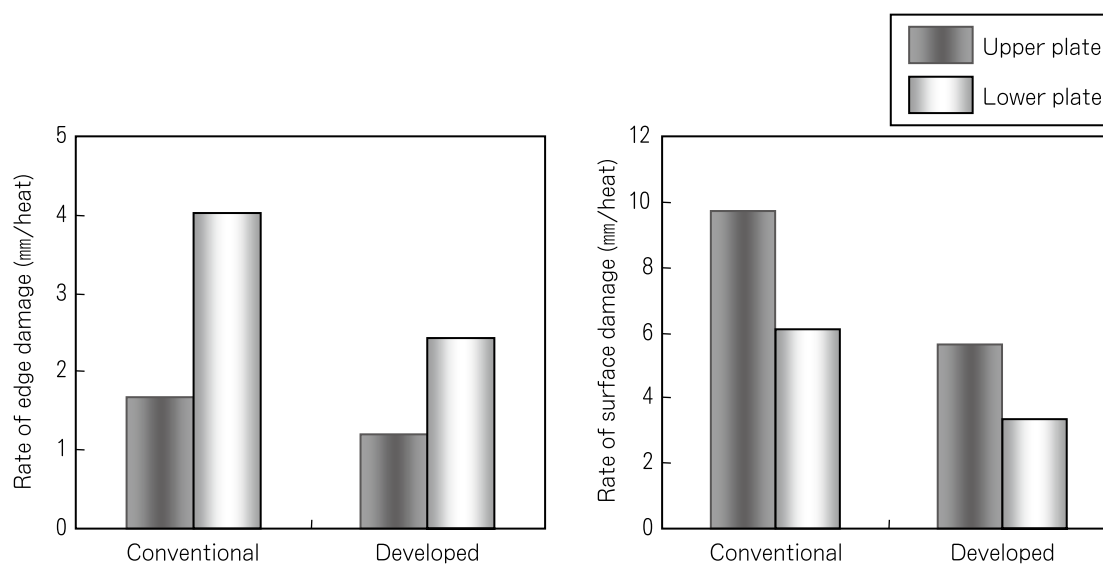


Fig. 6 Damage rate of SV plate at field trials.

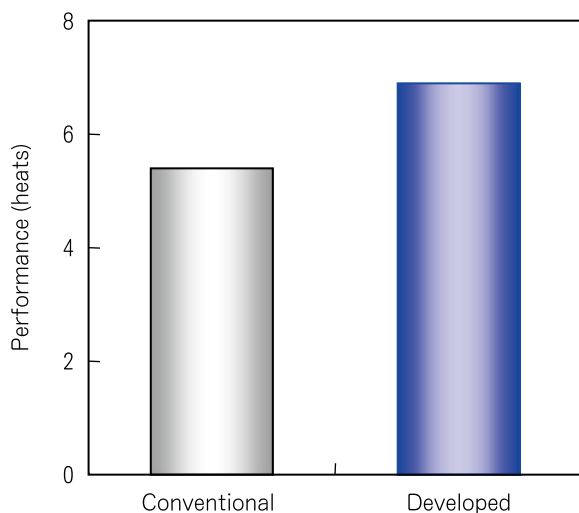


Fig. 7 Performance of SV plate at field trials.

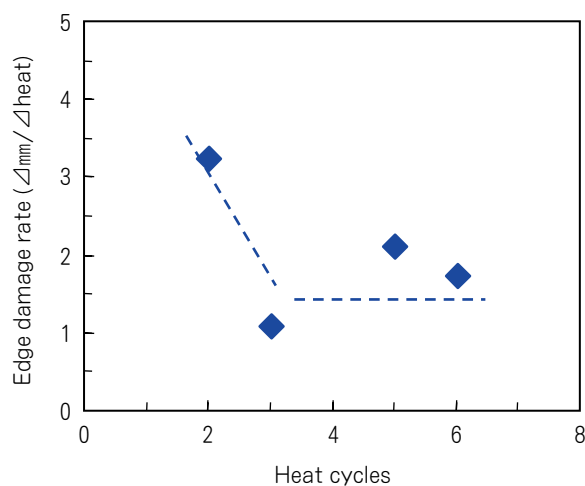


Fig. 9 Relationship between heat cycles and edge damage rate.

5 チャージで開発品を回収し、損傷状況と物性変化および添加した金属Alの形態変化を調査した。Fig. 8に使用回数と下プレートのエッジ損傷量との関係を示す。またFig. 9にチャージ毎のエッジ損傷速度の変化を示す。開発品のエッジ損傷速度は使用初期（2 チャージ）では大きく、使用中期～末期になると小さくなる傾向がある。

5. 2 使用回数増加に伴うSVプレート強度の変化

Fig. 10に、使用回数と下プレート内孔近傍の圧縮強さとの関係を示す。使用回数の増加に伴い、

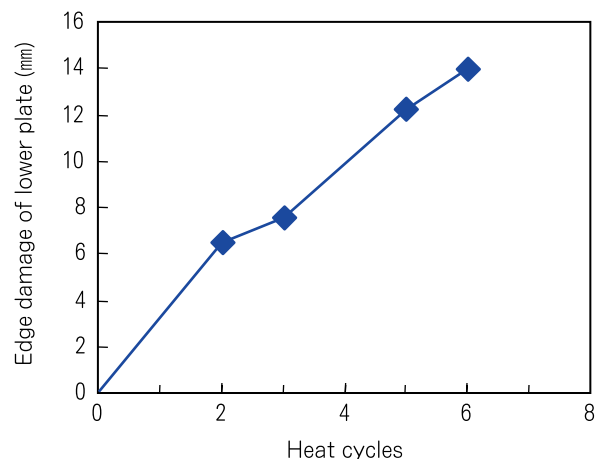


Fig. 8 Relationship between heat cycles and edge damage of developed lower plate.

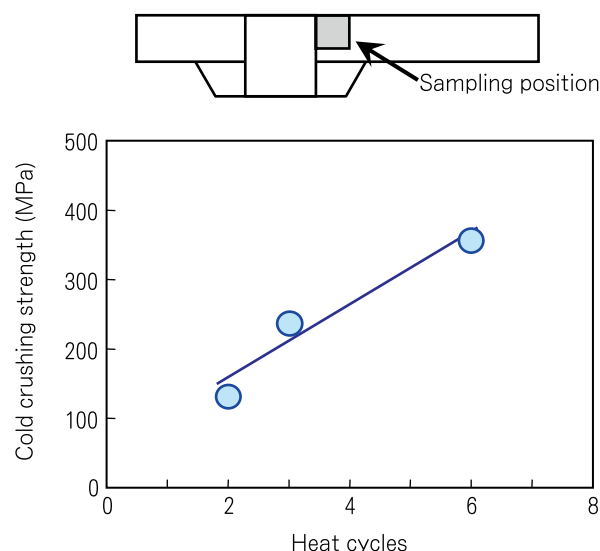


Fig. 10 Relationship between heat cycles and cold crushing strength of developed SV plate.

edge damage. Most of the bore edge damage occurs early in the casting sequence, with damage increasing only slowly in the middle and end of the sequence.

5. 2 Strength of SV plate with increasing heat cycles

Fig. 10 shows the relationship between heat cycles and cold crushing strength of developed material lower plate after use. The cold crushing strength increases with increasing heat cycles.

Fig. 11 shows cold crushing strength of the

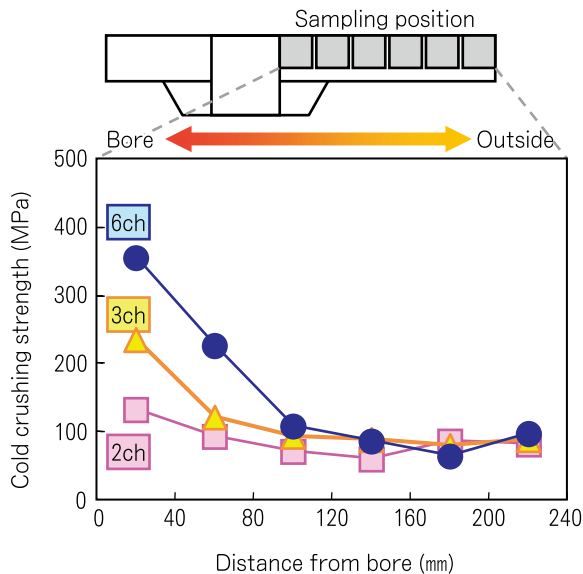


Fig. 11 Relationship between distance from bore and cold crushing strength of developed SV plate.

内孔近傍の圧縮強さが高くなっている。

Fig. 11に、下プレート内孔近傍から40mm角に分けて切り出した試料の圧縮強さの変化を示す。内孔に近いほど圧縮強さが高く、使用回数が多いほどその傾向が顕著である。

鋳造回数の増加に伴い内孔部の受熱量が増加し、強度が高くなることが判明した。

5. 3 使用回数増加に伴う添加Alの変化

Fig. 12に各使用回数後の稼働面近傍の微構造写真を、Fig. 13に使用回数と添加した金属Alの鋳物組成の変化を示す。

developed material lower plate after use at difference positions in the plate. The sample near the bore has high strength and this tendency is most remarkable for long sequences.

From these results, it was evident that the strength of the developed material increases according to the amount of heat received during long casting sequences.

5. 3 Changing of aluminum with heat cycles

Fig. 12 shows the microstructure around the bore of the developed plate after 2, 3, and 6 heats used. Fig. 13 shows the relationship between heat cycles and mineralogical changes in the aluminum.

As shown by the microstructure of the plate after 2 heats, aluminum has melted and diffused into the matrix, but metallic luster is still remaining. X-ray examination confirmed that Al remained as the metal. As the microstructure of the plate after 3 heats reveals, the metallic luster has disappeared and the matrix is transformed to a dense texture. The X-ray diffraction peak of aluminum in the sample taken after more than 3 heats has fallen sharply.

Fig. 14 shows SEM images of the developed SV plate after 6 heats and a conventional SV plate after 5 heats. It was observed that the

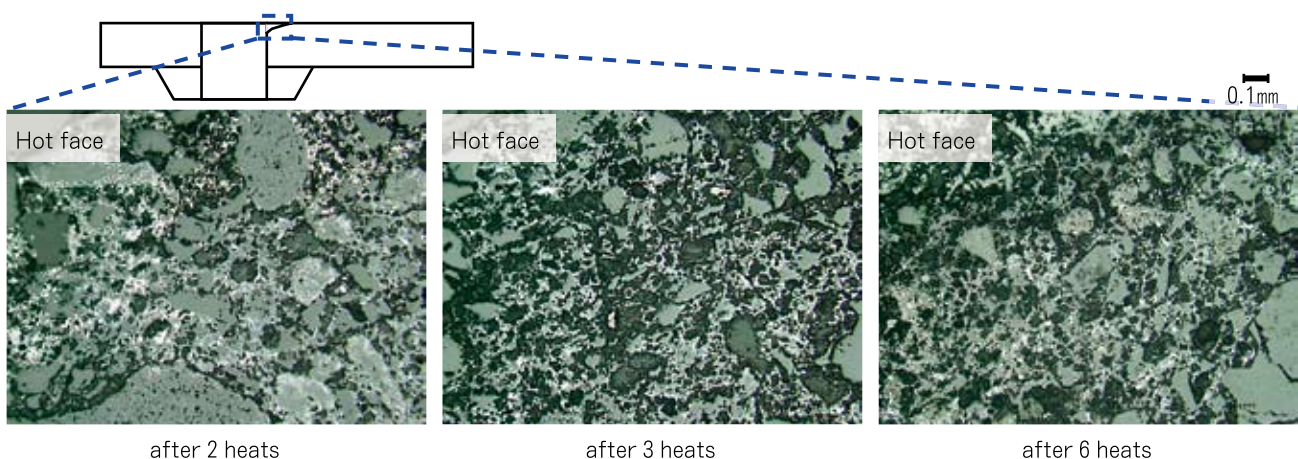


Fig. 12 Microstructures around bore of developed SV plates after used.

2 チャージ使用後品の微構造は、添加した金属 Al が軟化溶融し、マトリックス中へ拡散しているものの金属光沢が残っている。また X 線回折の結果からも、Al が金属として残存している。

3 チャージ使用後品の微構造は、金属光沢が消失し、マトリックスが緻密化した組織へと変化していることが観察された。X 線回折でも 3 チャージ使用後以降の試料においては、金属 Al の回折ピーク強度は急激に低下している。

比較品（5 チャージ使用後）と開発品（6 チャージ使用後）の SEM 像を Fig. 14 に示す。開発品は Al 成分が煉瓦マトリックス組織内に均一に拡散されており、金属 Al の増量により組織の緻密化が図れる効果が認められた。

5. 4 金属 Al の添加効果

開発品は使用初期にエッジ損傷の進行が大きく、使用中期から末期ではエッジ損傷の進行が抑制されている。マトリックス中では添加した金属

aluminum had diffused evenly into the matrix and changed to Al_2O_3 in the developed material. This increase in aluminum is effective in the

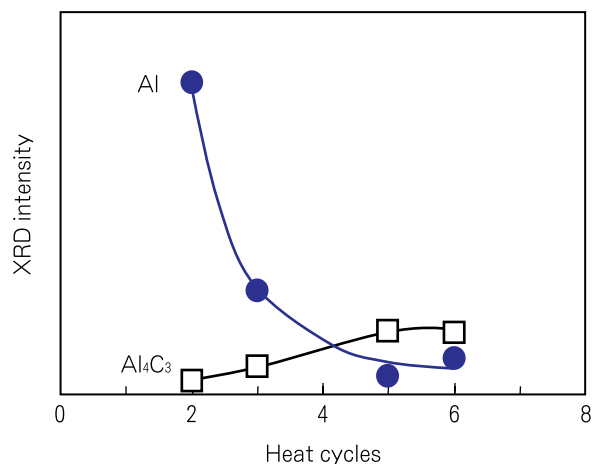
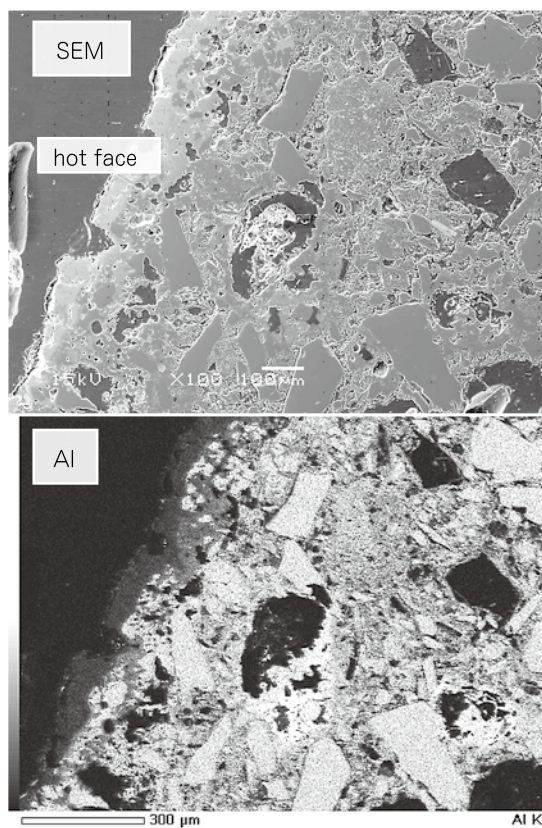
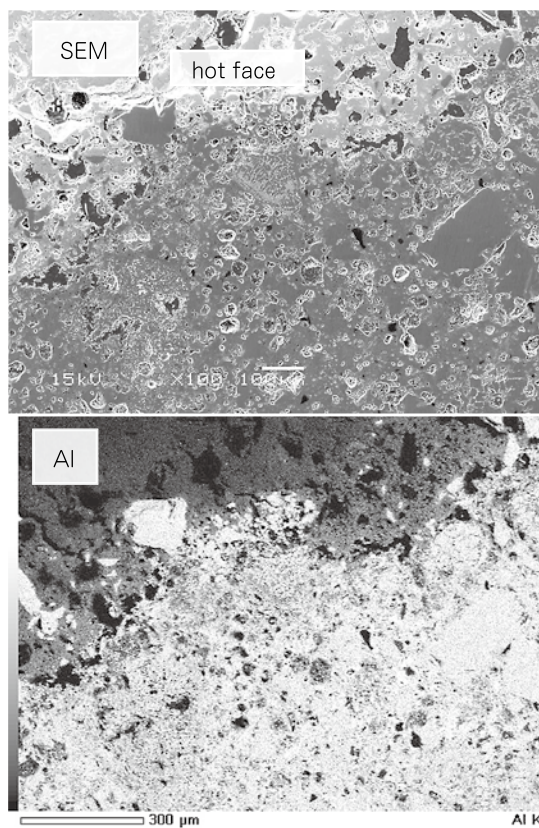


Fig. 13 Relationship between heat cycles and XRD intensity.



Conventional SV plate after 5 heats



Developed SV plate after 6 heats

Fig. 14 SEM images of SV plate after used.

Alは消失し、れんが組織を緻密化しており、使用回数の増加に従い使用後品の圧縮強さは高くなる。

カーボンを含有しているSVプレートは、 casting中の内気孔はCOまたはN₂ガスで満たされていると考えられる。その雰囲気下では、Fig. 15に示すように金属AlはAlN, Al₄C₃, Al-O-C-N系化合物等へ変化した後にAl₂O₃へ、または直接Al₂O₃へ変化¹⁾する。

今回、使用初期よりも使用中期から末期のエッジ損傷が低減した理由は、多量に添加した金属Alが casting時の受熱を経るごとにAl系炭化物、窒化物

densification of texture.

5. 4 Effect of aluminum

Bore edge damage in the developed SV plate material progressed in the early stages of the casting sequence. However, this progression of bore edge damage was successfully suppressed in the later stages. Cold crushing strength after use of the developed SV plate material increased with increasing heat cycles by means of densification of the texture through disappearance of aluminum from the matrix.

Shinagawa believes that the inside of the bore of SV plate was filled by CO or N₂ gas during casting. In this atmosphere, aluminum was changed to Al₂O₃ via AlN, Al₄C₃, and compound of Al-O-C-N as shown in Fig. 15.

We presume that the reduction of the bore edge damage at the middle and end of the sequence was due to densification of the texture and strengthening by means of the transformation of aluminum to Al₂O₃ via Al based carbides or nitrides by heating during casting.

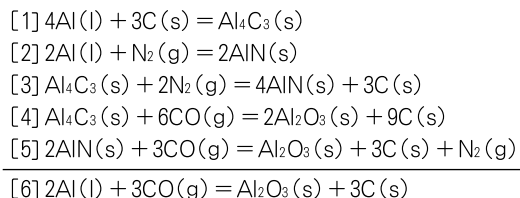
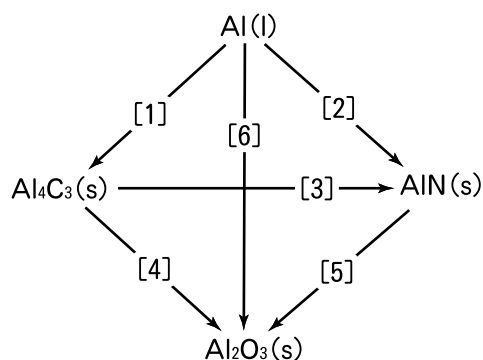


Fig. 15 Reaction of Al¹⁾.

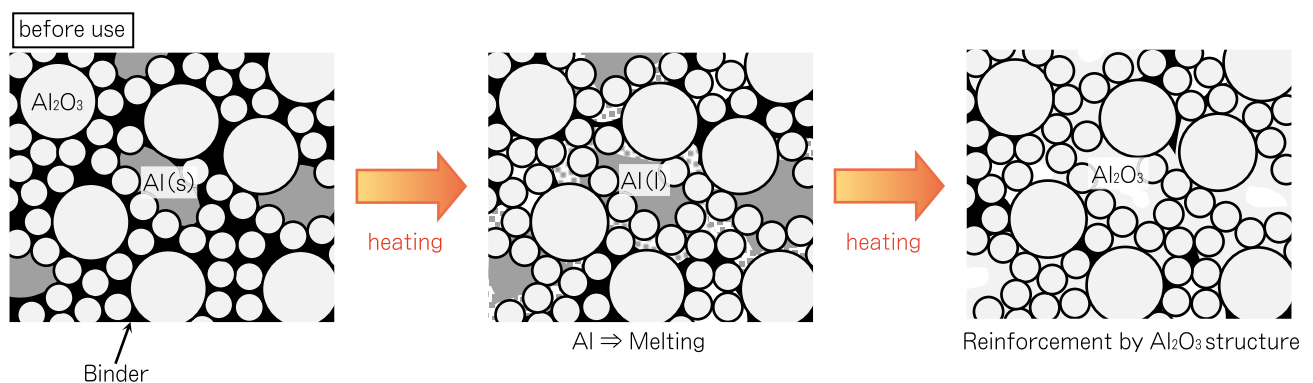


Fig. 16 Structure change model by heating.

から最終的には Al_2O_3 へと変化することによりれんが組織の緻密化，高強度化を促進していると考えられる（Fig. 16）。

6. まとめ

鑄造時の受熱に伴う金属Alの反応に着目し，金属Alを多量に添加したSVプレート用新材質を開発した。金属Alは Al_2O_3 微細組織へと変化し，れんがのマトリックス組織を緻密化する。実機使用した結果，エッジ損傷の低減が可能となり，耐用が30%向上した。

6. Conclusion

Shinagawa has developed a new unfired slide valve plate material by using aluminum. The matrix of the developed material is densified in service by means of the aluminum changing to Al_2O_3 . The new material shows 30% better performance in service compared with conventional material, primarily due to reduction in damage to the bore edge.

Reference

- 1) A. Yamaguchi : Inorganic Materials, Vol.4 (1997)