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塩基性プレート材質の耐スポーリング性改善

Improvement in Spalling Resistance of Basic Material for Slide Gate Plate

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品川技報

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要 旨

溶損鋼種用プレート材質として適用されることが多いMgO-C材質は、耐食性が高い一方で耐スポーリング性が低いという欠点がある。耐スポーリング性の向上には、スピネルなどの低膨張性原料を配合することが効果的であるが、その添加量の増加に伴って耐スポーリング性が向上する反面、耐食性は低下してしまう。これに対して、スピネルの配合粒度を粗粒側に調整することで、高耐食性でありながら耐スポーリング性を向上させた材質を開発することができた。

Abstract

MgO-C based materials are often used for the steel ladle and/or tundish slide gate plate treating corrosive steel due to its excellent corrosion resistance. Disadvantageously, the thermal spalling resistance of the materials is very poor. Although including low thermal expansion substances such as spinel improve the thermal spalling resistance, the corrosion resistance deteriorates if excessively large amount of spinel are added. Therefore, the influence of the grain size distribution of spinel was investigated. On the bases of the investigation, the corrosion resistance of high thermal spalling resistant MgO-C slide gate plate was successfully improved by utilizing coarse spinel aggregates.

1. 緒言

一般的に、プレート材質には耐スポーリング性と耐食性などの点から Al_2O_3 -C質が適用されているが、高酸素鋼やCa処理鋼などの受鋼により溶損が顕著となる^{1),2)}。そのため、これらの溶損鋼種に対してはMgO-C質など塩基性材質が適用されることがあるが³⁾⁻⁵⁾、これらは耐食性に優れる一方で耐スポーリング性に劣るという欠点がある。MgO-C質に対してスピネルを添加することで耐スポーリング性を改善することはできるが、スピネルの添加量によっては耐食性が大きく低下する

1. Introduction

Generally, Al_2O_3 -C based materials is used for the slide gate plate of steel ladle and/or tundish since it totally satisfies the properties required for slide gate plate such as thermal spalling resistance and corrosion resistance. However, corrosive steels such as high-oxygen or Ca-treated grade are noticeably corroded^{1),2)}. Therefore, basic material such as MgO-C is often applied to slide gate plate because of its excellent corrosion resistance³⁾⁻⁵⁾. On the

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Table 1 Mix ratio of spinel and magnesia, and properties of specimen

	Spl 0	Spl 20	Spl 50	Spl 100
Spinel / %	—	20	50	100
Magnesia / %	100	80	50	—
Apparent porosity / %	10.2	10.7	10.3	9.4
Bulk specific gravity	2.96	2.95	2.96	3.00

ため、これまでは添加量を抑えて耐スポーリング性よりも耐食性を優先していた。

今回、MgO-Spl-C質においてスピネル量およびスピネル粒度による耐食性、耐スポーリング性への影響を調査し、スピネルの多量添加によって耐スポーリング性を改善しながらも高い耐食性を有する材質を開発した。以下、その手法をスピネル量の影響および添加粒度の影響についてそれぞれ報告する。

2. スピネル量の影響

2. 1 供試試料

Table 1にマグネシアおよびスピネル量を示す。試料はMgO-C質をベースに、マグネシア骨材をスピネル骨材で20, 50, 100%置換した全4種類とした（以下、それぞれSpl 0, Spl 20, Spl 50, Spl 100と表記）。見掛け気孔率はいずれの試料も10%前後であり、成形性による影響が比較的小さくなるようにした。

Fig.1にスピネル量と物性値の関係を示す。1500℃での熱膨張率は1.4～2.2%で、スピネル量

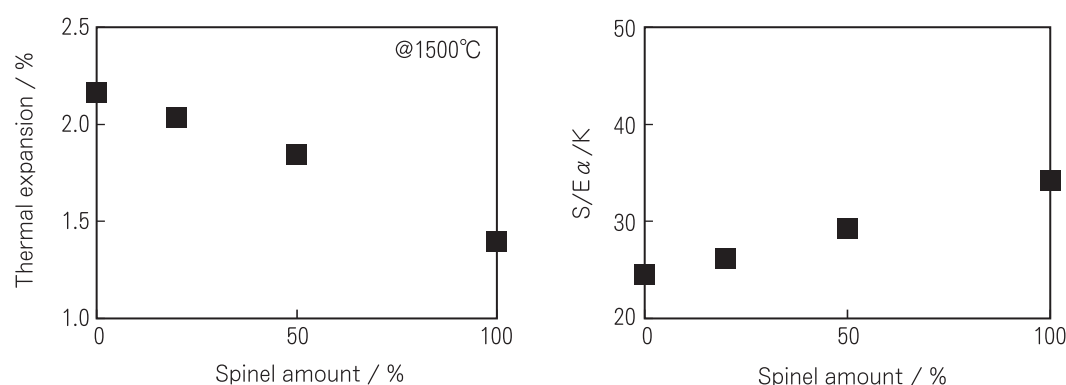
contrary, MgO-C based materials exhibits very poor thermal spalling resistance. In order to improve the thermal spalling resistance, including spinel is an effective means. While the thermal spalling resistance of MgO-C based materials becomes better as the spinel content increases, including excessive amount of spinel considerably deteriorates corrosion resistance. Thus, the amount of spinel addition had been limited since maintaining excellent corrosion resistance is the first priority required for MgO-C slide gate plates for facilities treating corrosive steel.

Regarding the above argument, we developed MgO-Spinel-C slide gate plate, which contains a large amount of spinel, that exhibits sufficient corrosion resistance. The good performance is attributable to optimal grain size distribution of the spinel aggregate. The influences of the amount and grain size of spinel on corrosion resistance and thermal spalling resistance is described below.

2. Influences of Spinel Amount

2. 1 Specimen preparation

Table 1 provides the magnesia and spinel mixing ratios associated with the apparent porosities and bulk specific gravities of the specimens. Four specimens of which the spinel contents

**Fig.1** Relation between spinel amount and properties of specimen.

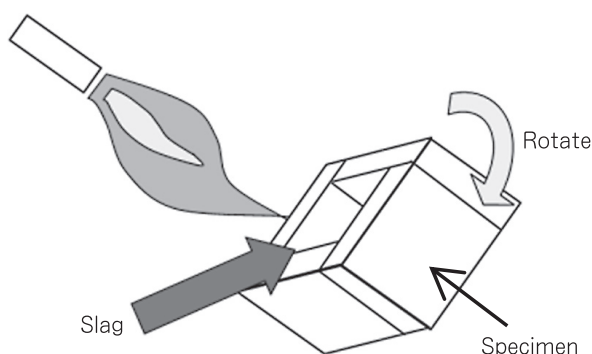


Fig.2 Schematic illustration of corrosion test.

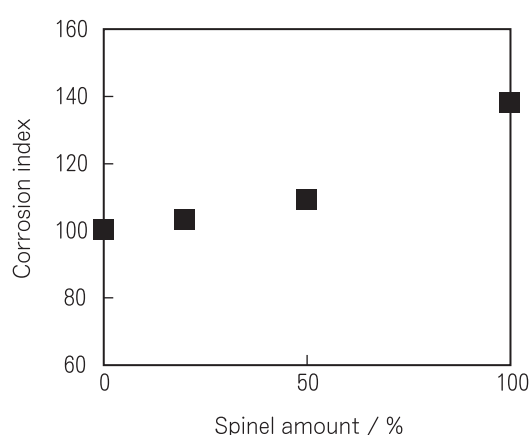


Fig.3 Corrosion index (Spl 0 = 100).

が多いほど低下した。耐熱スポーリング性を表す $S/E \cdot \alpha$ (S : 破壊強度, E : 弾性率, α : 熱膨張係数) はスピネル量が多いほど高くなり, 熱膨張率との相関が見られた。

2. 2 耐食性

侵食試験はプロパンバーナーを用いた回転るつぽ法で行った (Fig.2)。試料寸法は $L80 \times H60 \times W30$ mm で, 4 材質を張り合わせて, るつぽとした。試験は 1650°C で 5 時間行い, 1 時間ごとにスラグを交換した。スラグ組成は Ca 処理鋼を想定し, $\text{CaO} : \text{Al}_2\text{O}_3 : \text{FeO} = 35 : 35 : 30$ の組成を用いた。耐食性の評価には, 試料の高さ方向で 5 mm ごとに測定した試料の残厚から溶損量を求め, その平均値を Spl 0 を 100 として換算した溶損指数を用いた (数値が小さいほど耐食性が高いことを示す)。

Fig.3 に溶損指数を示す。耐食性は, スピネル量が多いほど低下し Spl 20, Spl 50, Spl 100 でそれ

were varied, as 0, 20, 50 and 100 in substitution for magnesia aggregate, were prepared. The specimens were denoted as Spl 0, Spl 20, Spl 50 and Spl 100, respectively. The apparent porosities of the specimens were approximately 10%. The difference of the apparent porosity among the specimens was small enough to neglect the influence of the packing degree on evaluation results.

Figure 1 shows variations of the evaluation results as a function of spinel amount. The thermal expansion at 1500°C linearly decreased from 2.2% to 1.4% with the increase in spinel content. The thermal spalling resistance can be evaluated by the index that consists of fracture strength; S , Young's modulus; E and thermal expansion coefficient; α , as $S/E\alpha$. A large $S/E\alpha$ indicates good thermal spalling resistance. As shown in Fig.1, $S/E\alpha$ increased proportionally to the spinel content, thus, the inverse correlation between $S/E\alpha$ and thermal expansion is obvious.

2. 2 Corrosion resistance

The corrosion resistance was evaluated by rotary slag test utilizing an oxygen-propane burner as shown in Fig.2. Four $L80 \times H60 \times W30$ mm rectangular specimens were assembled in a box shape to be subjected to the corrosion test, which was carried out at 1650°C for five hours. The composition of the corrosion agent was adjusted to $\text{CaO} : \text{Al}_2\text{O}_3 : \text{FeO} = 35 : 35 : 30$, which was equivalent to the slag composition of Ca-treated grade steel. The slag was exchanged every hour in order to maintain the corrosivity. The post corrosion test specimens were cut along the center line followed by a corrosion thickness evaluation, which was determined by the average value of residual thickness at intervals of 5mm. The results of the corrosion test are expressed by the corrosion index of which the corrosion

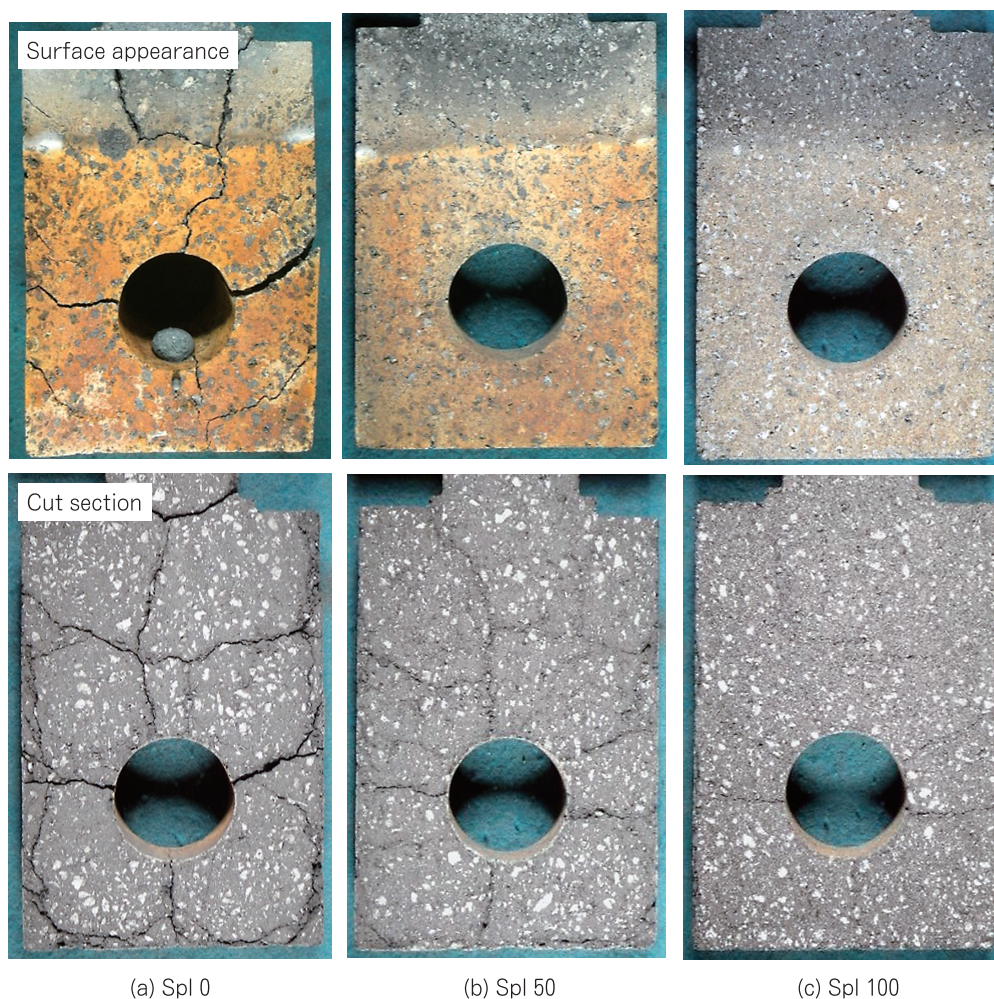


Fig.4 Surface appearance and cut section of specimens after spalling test.

ぞれ 3, 9, 38%低下した。

2. 3 耐スポーリング性

耐スポーリング性の評価は、1550℃程度の溶鉄に試料を1分間浸漬した後空冷する方法で、Spl 0, Spl 50, Spl 100の3材質について行った。試料サイズはL70×H110×W40mmで、下部中央にφ30mmで穿孔された形状を用いた。試験後試料は厚み方向の中心線で切断し、切断面の亀裂長さを測定して比較した。

Fig.4に試験後試料の外観および切断面を示す。亀裂はスピネル量が多いほど少なく、不明瞭であった。Spl 50, Spl 100は試料表面では亀裂がほとんどみられなかったが、Spl 0は試料表面にまで亀裂が達して破断した。

thickness of Spl 0 was regarded as standard, thus, the corrosion resistance becomes better as the corrosion index decreases.

Figure 3 shows the corrosion index as a function of spinel content. Corrosion resistance deteriorated for 3, 9 and 38 with the increase in spinel content of 20, 50 and 100.

2. 3 Thermal spalling resistance

The thermal spalling resistance was evaluated for Spl 0, Spl 50 and Spl 100. Plate shape specimens of L70×H110×W40mm to which bore of 30mm in diameter had been drilled were immersed in molten pig iron controlled at 1550℃ in an induction furnace for one minute

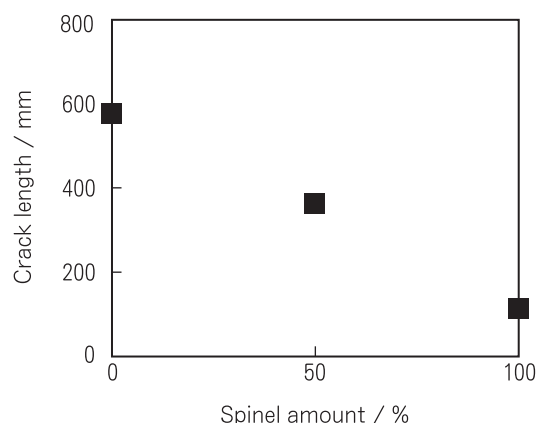


Fig.5 Relation between spinel amount and crack length of specimen after spalling test.

Table 2 Features of spinel grain size distribution, and properties of specimens

	1	2	3	4 (Spl 50)	5
Spinel / %	50				
Magnesia / %	50				
Index of spinel grain size distribution	1.0	1.7	2.6	6.0	7.2
Apparent porosity / %	9.9	9.3	11.1	10.3	11.2
Bulk specific gravity	2.99	3.00	2.95	2.96	2.94

Fig.5に亀裂長さの測定結果を示す。切断面写真からもわかるようにスピネル量が多いほど亀裂長さは短かった。

3. スピネル粒度の影響

3. 1 供試試料

Table 2にスピネル粒度の特徴を示す。試料はスピネル50%品（第2節のSpl 50がNo.4に相当）をベースに、スピネルの配合粒度を変化させた全5種類とした。スピネル粒度指数は、スピネル骨材のみの粒度分布を計算し、そのうちミディアン径が最も細かい配合を1として指数化した。スピネル粒度指数が小さいほどスピネル骨材の添加粒度が細かく、マトリックス中のスピネル比率が高くマグネシア比率が低くなることを示す。

Fig.6にスピネル粒度と物性値の関係を示す。1500℃での熱膨張率は1.7～1.9%で、中間的な粒度

followed by natural cooling. The post spalling test specimens were sliced along the center line in the width direction followed by measurements of crack length on the cross section.

Figure 4 shows external appearances and cross sections of the specimens after the spalling test. Obviously, cracks become thinner and scarcer as spinel content increases. Although cracks were seldom recognized on the external surfaces of Spl 50 and Spl 100, Spl 0 was fractured as a result of a crack reaching the external surface. Figure 5 shows the variation in crack length as a function of spinel content. The influence of spinel amount on thermal spalling was quantified.

3. Influences of Spinel Grain Size Distribution

3. 1 Specimen preparation

Table 2 summarizes the characteristics of spinel grain size as well as apparent porosities and bulk specific gravities. Five spinel aggregates, of which the grain size distributions were varied, were used for specimens containing 50% spinel. No. 4 was identical to Spl 50 in section 2. The index of spinel grain size distribution indicates the median diameter standardized by that of the finest spinel aggregate. Hence, spinel content in the matrix increases as the index decreases.

Figure 6 shows the variation of thermal expansion at 1500℃ and $S/E\alpha$ as a function of the index of spinel grain size distribution. The thermal expansion at 1500℃ ranges between 1.7 and 1.9%, at which the maximum value is estimated to be around the index of spinel grain size distribution of 4. The $S/E\alpha$ decreases as the index of spinel grain size distribution increases.

3. 2 Corrosion resistance

The corrosion resistance was evaluated for

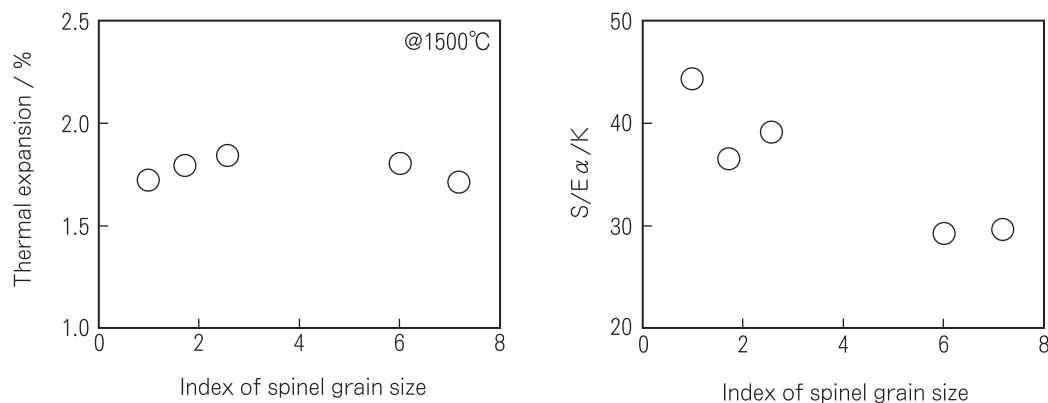


Fig.6 Relation between index of spinel grain size distribution and properties of specimens.

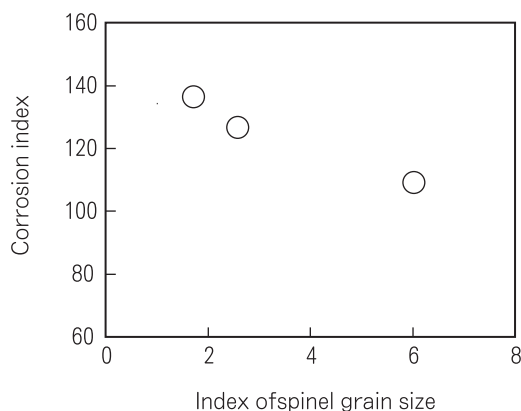


Fig.7 Corrosion index (No.4 = Spl 50 = 109).

(スピネル粒度指数で4程度)で極大となるような傾向が認められた。耐熱スポーリング性を表す $S/E\alpha$ はスピネル粒度が粗いほど低下した。

3.2 耐食性

侵食試験は上記(第2.2項)同様に行い、No.1～4の4材質を比較した。溶損指数は、第2.2項と共通のNo.4 (Spl 50) を109として指数化した。

Fig.7に溶損指数を示す。耐食性は、スピネル粒度が細かいほど低下し、Spl 0に比べてNo.1, 2, 3でそれぞれ34, 36, 26%低下した。

3.3 耐スポーリング性

耐スポーリング性の評価も上記(第2.3項)同様に行い、No.1, 3, 4を比較した。

Fig.8に試験後試料の外観および切断面を示す。亀裂は全体的に少なく、比較的不明瞭であった。

specimens No. 1 to 4 under identical conditions with those described in subsection 2.2. The corrosion index was standardized regarding the corrosion thickness of No. 4 (Spl 50) as 109 in order to directly compare the results of two corrosion tests.

Figure 7 shows the corrosion index as a function of the index of spinel grain size distribution. The corrosion resistance deteriorated with the decrease in the index of spinel grain size distribution. The deterioration degree of No. 1, 2 and 3 were compared to Spl 0 were 34, 36 and 26%, respectively.

3.3 Thermal spalling resistance

Thermal spalling resistances of specimens No. 1, 3 and 4 were evaluated in an identical procedure to that described in subsection 2.3. Figure 8 shows the external appearances and cross sections of the specimens after the thermal spalling test. The degree of cracking in all specimens was slight. No notable cracks were observed in any specimens. Figure 9 shows the crack lengths on the cross sections of the specimens after the test. The crack length becomes shorter with the decrease in the spinel grain size distribution index. The difference among three specimens is small.

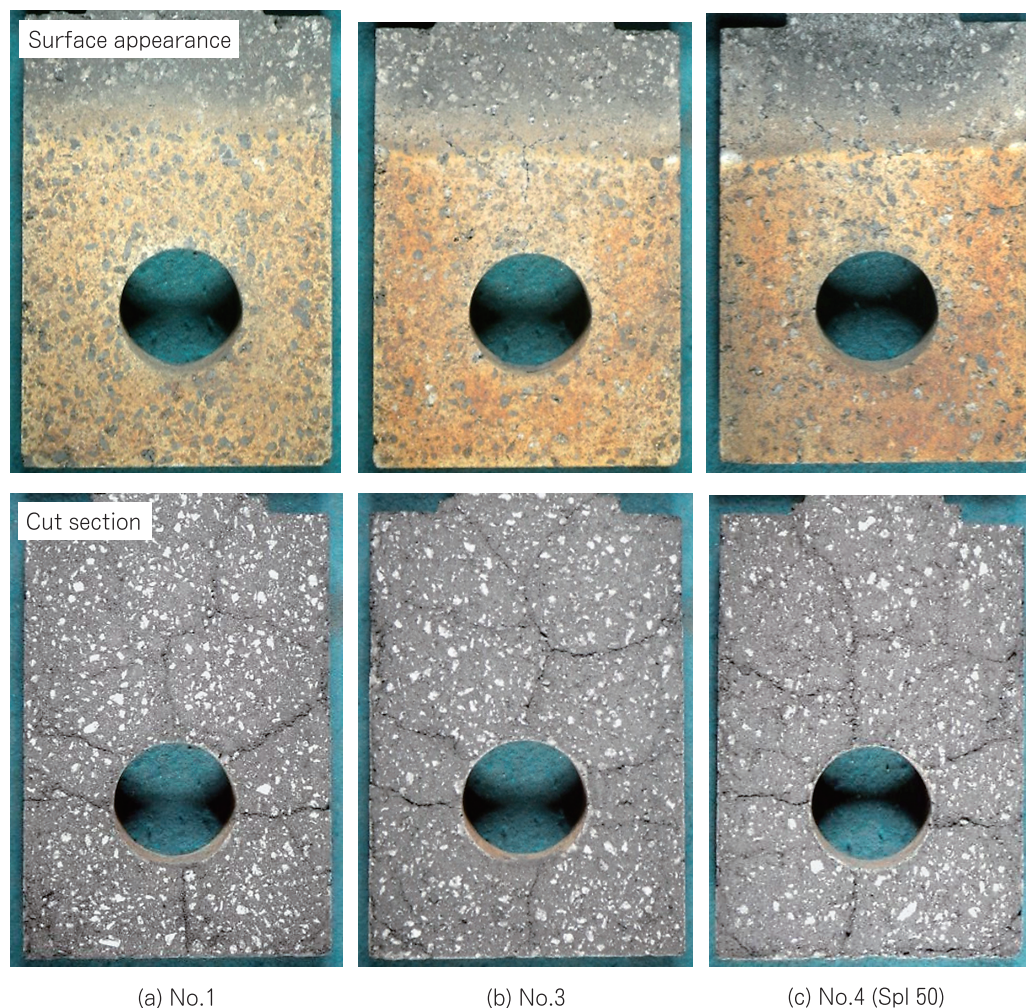


Fig.8 Surface appearance and cut section of specimens after spalling test.

いずれの試料も試料表面には目立った亀裂はなかった。

Fig.9に亀裂長さの測定結果を示す。スピネル粒度による差は小さいが、添加粒度が細かいほど亀裂長さは短かった。

4. スピネル多量添加による高耐食性・ 高耐スポーリング性プレート材質

Fig.10, 11にスピネル量と粒度の影響の結果を合わせて、スピネル量と耐食性の関係および1500℃熱膨張率と亀裂長さの関係をそれぞれ示す。

MgO-Spl-C質の耐食性は、スピネル量に対して線形に変化するのではなく、スピネル粒度による

4. Improvement in Corrosion and Spalling Resistance of Basic Material Containing Large Amount of Spinel Aggregates for Slide Gate Plates

Figures 10 and 11 integrally show the influence of spinel content on the corrosion index and variation in crack length after the spalling test as a function of thermal expansion at 1500℃, respectively. According to Fig.10, it is clarified that the corrosion resistance of MgO-Spl-C based materials is considerably deteriorated by reduction in the grain size of spinel as well as increase in amount of spinel. This is considered

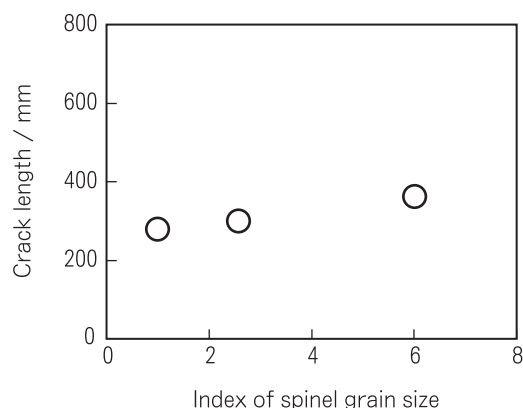


Fig.9 Relation between spinel grain size distribution and crack length of specimens after spalling test.

影響が非常に大きかった (Fig.10)。メカニズムとしては、マトリックス中のスピネル量が多いほど (マグネシア量が少ないほど) 溶損されやすいため耐食性が低下したと考えられる。

一方で、耐スポーリング性はスピネル粒度の影響が比較的小さく (Fig.11), 1500℃での熱膨張率にほぼ比例する。熱膨張率はスピネル量に大きく依存し、添加量が多いほど熱膨張率が小さくなるので耐スポーリング性も向上した。

以上より, MgO-C質へのスピネル添加は, スピネル粒度を調整することで耐食性をMgO-C質と同等に維持しながら, 耐スポーリング性を大幅に改善できることがわかった。

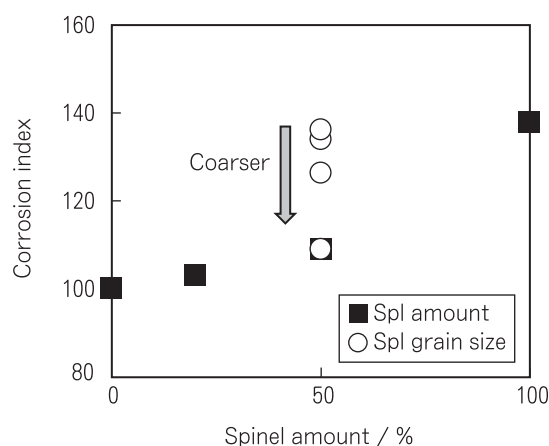


Fig.10 Influence of spinel amount and grain size distribution on corrosion.

attributable to the reduction of MgO fraction in matrix part.

On the other hand, while including large amount of spinel markedly improves the thermal spalling resistance, spinel grain size distribution was evaluated to have only a small effect on thermal spalling resistance as shown in Fig. 11. Figure 11 indicates that thermal expansion is the dominant factor influencing thermal spalling resistance and the influence of spinel grain size distribution on thermal expansion is practically negligible.

Hence, it was found that the application of a large amount of grain size optimized spinel considerably improves the thermal spalling resistance, minimizing the adverse influence of spinel on corrosion resistance.

5. Conclusion

It is generally accepted that the addition of spinel to MgO-C based materials for the slide gate plate, which show superior corrosion resistance and poor thermal spalling resistance, improves thermal spalling resistance, while it deteriorates corrosion resistance. According to the investigation, however, it was clarified that the optimization of spinel grain size distribution

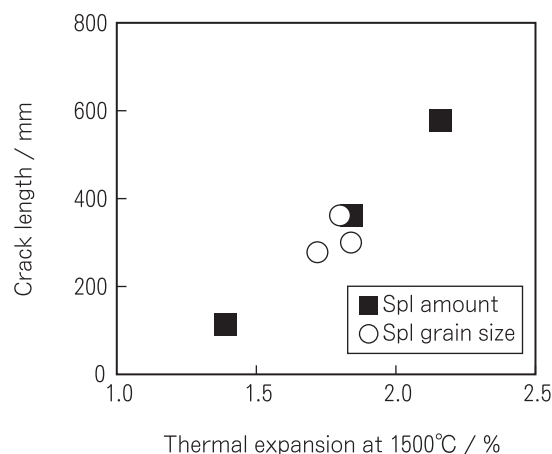


Fig.11 Relation between thermal expansion and crack length after spalling test.

5. まとめ

高耐食性, 低耐スポーリング性であるMgO-C質にスピネルを添加すると, 耐スポーリング性は向上するが耐食性は低下することが一般的である。しかし, スピネルの配合粒度を粗粒側に調整することで耐スポーリング性を向上させながら耐食性の低下を抑制することができる。

minimizes the deterioration of corrosion resistance. Thus, it was concluded that considerable improvement in thermal spalling resistance and minimization of the deterioration of corrosion resistance is possible by using a large amount of grain size optimized spinel aggregates.

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