[Technical Report]

無予熱高耐用鋳造ノズルの開発

Development of the Preheating-Free High-Durability Casting Nozzle

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要　旨

化学成分の調整に依らず，耐火物の気孔形態の制御による低膨張化技術を適用して，低膨張で緻密質なアルミナ−グラファイト（AG-N），マグネシア−グラファイト（MG-N），スピネル−グラファイト（SPG-N），ジルコニア−グラファイト（ZG-N）4種の新材質を開発した。新材質はシリカや炭素などの溶損しやすい骨材を最少にした上で，組織の緻密化，耐火物内部の気孔形態を制御することで低膨張化が可能となり，高耐食性と優れた耐熱衝撃性とを兼備する特徴を有している。近年増加している，Ca処理鋼などの侵食性の強い鋼種，特殊鋼に対する高耐食化ニーズへの対応材として期待される。また，鋳造用ノズルの無予熱化は，予熱用燃料コストの削減やCO_2ガス発生の抑制に繋がり，今後のカーボンニュートラルの実現に向けた環境負荷低減技術の1つとして貢献可能と考えている。

Abstract

By applying the thermal expansion lowering technology by controlling the pore morphology of refractories without adjusting the chemical composition, four new materials with low expansion and high density were developed: alumina-graphite (AG-N), magnesia-graphite (MG-N), spinel-graphite (SPG-N), and zirconia-graphite (ZG-N). The new material has features of both high corrosion resistance and excellent thermal shock resistance by minimizing amount of the easy melt aggregate such as silica and carbon, and lowering the expansion by densifying the structure and controlling the pore morphology form inside the refractories. It is expected as a material for coping with the needs of high corrosion resistance for steel with strong corrosiveness such as Ca treated steel, which has been increasing production recently. In addition, the preheating-free casting nozzle leads to reduction of fuel cost for heating as well as suppression of both heat and CO_2 gas generations. Actual used of such nozzle can contribute as one of the environmental loading reduction technologies in the steel industry for realization of carbon neutrality in future.

1　緒言

ロングノズルや浸漬ノズルに代表される連続鋳造用ノズルは，エアーシール（断気）機能が特に重要で，鋳造中に割れてはならない耐火物である。これまで連続鋳造用ノズルの割れを防止するため，さまざまな対策が取られてきた。たとえば，材質面では，低熱膨張溶融シリカや高熱伝導性黒鉛原料などをアルミナやジルコニアなどの耐食性骨材とともに適量ブレンドして，熱衝撃に強い鋳造用ノズルが製造されている。一方でシリカや黒鉛原料は，溶融スラグや溶鉄に対する耐食性が低く，その添加量の増加に従い耐用が低下する問題がある。このため，操業側で事前にノズルの予熱を行い，溶融シリカや黒鉛原料の添加量を減じて，割れを防止しつつ，耐用を向上させてきたのが現状である。

1 Introduction

Nozzles for continuous casting represented by long nozzles and submerged entry nozzles are refractory which air seal function is especially important and should not break during casting. Until now, various countermeasures have been taken to prevent cracking of nozzles for continuous casting. For example, as a countermeasure on material, an appropriate amount of fused silica with low thermal expansion and high thermal conductivity graphite raw materials are blended together with corrosion resistant aggregates such as alumina and zirconia to produce a casting nozzle with improved thermal shock resistivity. On the other hand, silica and graphite raw materials have poor corrosion resistance against both molten slag and iron, and have a problem that their durability deteriorate with increasing the amount of their addition. Therefore, in the present state, the nozzle was preheated in advance in the operation side, resulting in a certain improvement on the durability, while the cracking is prevented due to reduce

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黒崎播磨(株)技術研究所では，従来の溶融シリカや黒鉛添加による割れ防止策に依らない方法で，低カーボン質で低膨張な炭素含有耐火物の開発を進めてきた。本報では，予熱をほとんど必要としない数種の高耐用なノズル材質の特徴について紹介する。

2　新規開発した４種の鋳造用ノズル材質

耐熱衝撃性と耐食性を両立させたアルミナ－グラファイト材質（以下 AG-N），マグネシア－グラファイト材質（以下 MG-N）[1,2]，スピネル－グラファイト材質（以下 SPG-N），ジルコニア－グラファイト材質（以下 ZG-N）の４種類の新規材質を開発した。新規開発材質は，シリカや炭素などの溶損性骨材を最少にした上で，組織の緻密化，耐火物内部の気孔形態の制御により，低膨張化を実現することが可能となった。**Table 1** に，新規に開発した無予熱ノズル用本体材質（AG-N, MG-N, SPG-N）と一般汎用本体材質（AG, ASG）の化学成分及び品質比較を示す。比較用材の従来 AG 材質は耐食性指向のノズル内張り用材質であり，アルミナ－シリカ－グラファイト（以下 ASG）材質は無予熱で使用可能な耐熱衝撃指向のノズル本体用材質である。新規開発材質（AG-N,MG-N,SPG-N）は，従来の耐食性指向材 AG と同様な構成成分であるが，見掛け気孔率が 15 ％以下と緻密質で，従来材質（AG, ASG）より低熱膨張率で優れた耐熱衝撃破壊抵抗係数（$R = S/E{\cdot}\alpha$, S: 曲げ強度, E: 弾性率, α: 1000 ℃における熱膨張率）を示している。また，**Table 2** には，パウダーライン用 ZG の開発材質(ZG-N)と汎用材質（ZG-1, ZG-2）の化学成分及び品質比較を示す。パウダーライン材質については，比較材質 ZG-1 は，汎用材として使用されている高ジルコニア含有量 82 mass％の耐食性指向材質であり，比較材質 ZG-2 は，ジルコニア含有量 77 mass％の耐熱衝撃性指向汎用材質である。一方，新規開発材質 ZG-N は，ジルコニア含有量が ZG-1 と同等で，ZG-2 とほぼ同等な低膨張性を有し，優れた耐熱衝撃破壊抵抗係数（R）を示している。また，ZG 材質開発品の見かけ気孔率は 14 ％以下であり，従来汎用 ZG 材質よりも緻密な組織となっている。

the both amount of fused silica and graphite raw materials.

In the technical laboratory of Krosaki Harima Corporation, the development of a low carbon type carbon containing refractory with low thermal expansion has been advanced by a method different from the conventional one with crack prevention due to both fused silica and graphite additions. This paper introduces the features of several kinds of newly developed high durable materials for molten steel teeming nozzle with requiring little preheating.

2 Four newly developed nozzle materials for steel continuous casting

Four-kind of new materials were developed: alumina-graphite material (hereinafter AG-N), magnesia-graphite material (hereinafter MG-N[1,2]), spinel-graphite material (hereinafter SPG-N), and zirconia-graphite material (hereinafter ZG-N), with both high thermal shock and corrosion resistances. In the newly developed material, it became possible to realize the low thermal expansion by densifying the structure and controlling the morphology of pore inside the material, while the easy-erosive aggregates such as silica and carbon were minimized. The composition and physical properties of the newly developed nozzle body material (AG-N, MG-N, SPG-N) for non-preheating are compared to those of the general-purpose body material (AG, ASG) in **Table 1**. The conventional AG material in the comparison, with high corrosion resistance, was used as nozzle lining, and alumina-silica-graphite (hereinafter ASG) with high thermal spalling resistance, was used for non-preheating nozzle body. The newly developed materials (AG-N, MG-N, SPG-N) have similar composition to the conventional corrosion-resistant oriented material AG, they exhibited lower thermal expansion property with an excellent thermal shock fracture resistance than the conventional material, they were densified with 15 % or less apparent porosity. **Table 2** shows the same composition as **Table 1** between the developed ZG material and the general-purpose conventional products for powder line. The comparison materials ZG-1 with zirconia content of 82 mass%, and the ZG-2 with zirconia content of 77 mass%, were used as general-purpose materials specified for high corrosion resistance and high thermal spalling resistance, respectively. On the other hand, the newly developed material ZG-N, has low thermal expansion property equivalent to the ZG-2 in spite of the same zirconia content as ZG-1, resulting in excellent thermal shock fracture resistance coefficient (R). The apparent porosity of the ZG-N was lower than 14 %, and the structure was denser than the conventional ZG materials.

Table 1 Composition and physical properties of the body materials

Sample Composition & properties		AG-N	MG-N	SPG-N	AG	ASG
		Newly developed			High corrosion resistant	High thermal spalling resistant
Composition / mass%	Free C	18	19	19	18	25
	SiO_2	5	3	3	4	24
	Al_2O_3	76	-	56	77	45
	MgO	-	77	21	-	-
	Others	1	1	1	1	3
Apparent porosity / %		14.8	15.0	12.2	17.5	15.6
Thermal expansion at 1000 ℃ / %		0.23	0.24	0.23	0.33	0.23
R (=S/E・α)		4666	5100	4472	2987	4292

Table 2 Composition and physical properties of the powder line materials

Sample Composition & properties		ZG-N	ZG-1	ZG-2
		Newly developed	High corrosion resistant	High thermal spalling resistant
Composition / mass%	Free C	13	13	19
	ZrO_2	82	82	77
	Others	5	5	5
Apparent porosity / %		13.8	17.1	16.1
Thermal expansion at 1000 ℃ / %		0.27	0.38	0.26
R (=S/E・α)		4418	2458	4369

3　新規開発材質の特性比較

3・1　耐スポーリング性評価

各材質の耐スポーリング性の評価法は，**Fig. 1** に模式的に示すように外周側からの冷却とするため底蓋付き円筒形状（外径 115 mm ×内径 45 mm ×高さ 70 mm）試験片を，1300 ～ 1500 ℃の各温度に 1 h 加熱保持後，直ちに流水中に 3 min 間浸漬し急冷する水冷法より行った。試験後，試験片の亀裂発生有無を切断により観察し，試験結果を **Table 3** に示す。結果として，低膨張特性を示すノズル本体用 AG-N，MG-N，SPG-N が，ΔT ＝ 1500 ℃までの試験にて亀裂の発生がなく，従来の無予熱仕様の ASG 材質のそれと同等レベルの耐スポーリング性であることを確認した。この結果は，新規開発材質の熱膨張率が，従来無予熱用 ASG 材質と同程度の低い値であることにより得られたと考えている。

3 Characterigation of newly developed materials

3・1 Evaluation of spalling resistance

As a method for evaluating the spalling resistance of each material, test was carried out by the water cooling method. As shown schematically in **Fig. 1**, in the test, for cooling from the outer periphery, a cylindrical shape specimen with a bottom lid (outer diameter 115 mm × inner diameter 45 mm × height 70 mm) and was heated to and held at predetermined temperatures for 1 h, then immediately quenched and immersed in running water for 3 min. After the test, the presence or absence of cracks was checked face of cutting in the specimen. The spalling test results by the water-cooling method are shown in **Table3**, in which the developed AG-N, MG-N and SPG-N for the nozzle body material showed low thermal expansion characteristics, resulting in an equivalent spalling resistance to the conventional ASG material for non-preheating specifications without cracking in the test water cooling method up to 1500 ℃.

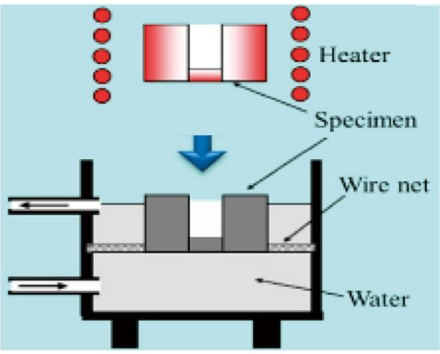

Fig. 1 Schematic illustration of spalling test3).

Table 3 Spalling test results of the refractory specimens for ΔT=1300～1500℃

Sample ΔT / ℃	AG-N	MG-N	SPG-N	AG	ASG
	Newly developed			High corrosion resistant	High thermal spalling resistant
1300	○	○	○	○	○
1400	○	○	○	×	○
1500	○	○	○	―	○

○：clear ×：crack

3・2 ノズル本体用材質の溶融スラグに対する耐食性評価

各材質について，塩基度の異なるスラグに対する耐食性を **Fig. 2** に示すように鋼浴上の溶融スラグ中へ浸漬する方法にて評価した。浸漬試験は，低炭鋼を1550 ± 10 ℃まで高周波誘導炉により加熱溶融した後，溶融スラグ厚さが約 20 mm になるように所定のスラグを投入した。供試材は，開発材 3 種と比較材 ASG 材質 1 種の合計 4 種を同時に，溶鋼直上で 5 min 保持後，所定時間溶鋼中へ浸漬した。スラグの塩基度 $CaO / SiO_2 \fallingdotseq 1$ 及び 3 の 2 種類のスラグ組成に対する耐食性の評価を行った5)。結果として，試験後の溶鋼／スラグ界面での最大溶損深さを計測し，比較材 ASG を 100 とした場合の各サンプルの溶損指数を各塩基度に対して比較して **Fig. 3** に示した。また，**Fig. 4** には浸漬試験後のサンプルの外観写真をスラグの各塩基度ごとに示した。以上の結果より，溶損指数は ASG ＞ MG-N ＞ AG-N ＞ SPG-N の順で小さくなり，いずれの塩基度においても，ASG 材質の溶損速度が高く，SPG-N 材質は比較的健全で，溶損指数も最も低い値であり，スラグと接触可能性のある部位の耐用向上のために，SPG-N 材質適用が有効であることが判明した。

3.2 Corrosion resistance against molten slag

For each material, the corrosion resistance against slag with different basicity was evaluated by the method of immersing into molten slag floating on a steel bath as shown in **Fig. 2**. In the immersion test, the low-carbon steel was heated and melted by the high frequency induction furnace up to 1550 ± 10 ℃, and then the prescribed slag was added so that the molten slag thickness became about 20 mm. Three kinds of developed and one kind of conventional ASG, totally 4 materials were immersed simultaneously into the steel bath in a prescribed time after being held at the upper position of the steel bath for 5 min. The corrosion resistance of each material was evaluated with the slag compositions of $CaO / SiO_2 \fallingdotseq 1$ and 3, respectively5). The evaluation was performed by measuring and comparing the maximum melting depth in the specimen at the molten steel / slag interface after the test. In **Fig. 3**, the corrosion indexes for each sample in the immersion tests with two-kind of basicity were shown when the index for material ASG was set to 100. **Fig. 4** shows the appearance of specimen after the test. From the results shown in the figures, the corrosion index decreased in the order of ASG > MG-N > AG-N > SPG-N, for both basicity, and the index was highest for the ASG material and lowest for SPG-N material with relatively sound appearance. The results obtained apparently indicated that the application of SPG-N material to the part possibly contacting with the slag must be effective for the durability improvement of the nozzles.

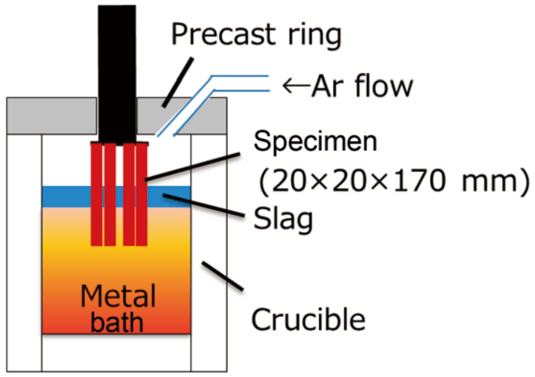

Fig. 2 Schematic illustration of slag corrosion test[4].

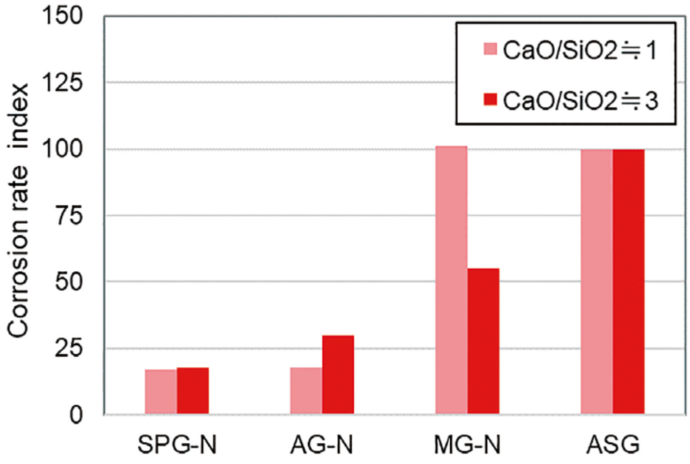

Fig. 3 Results of the slag corrosion test.

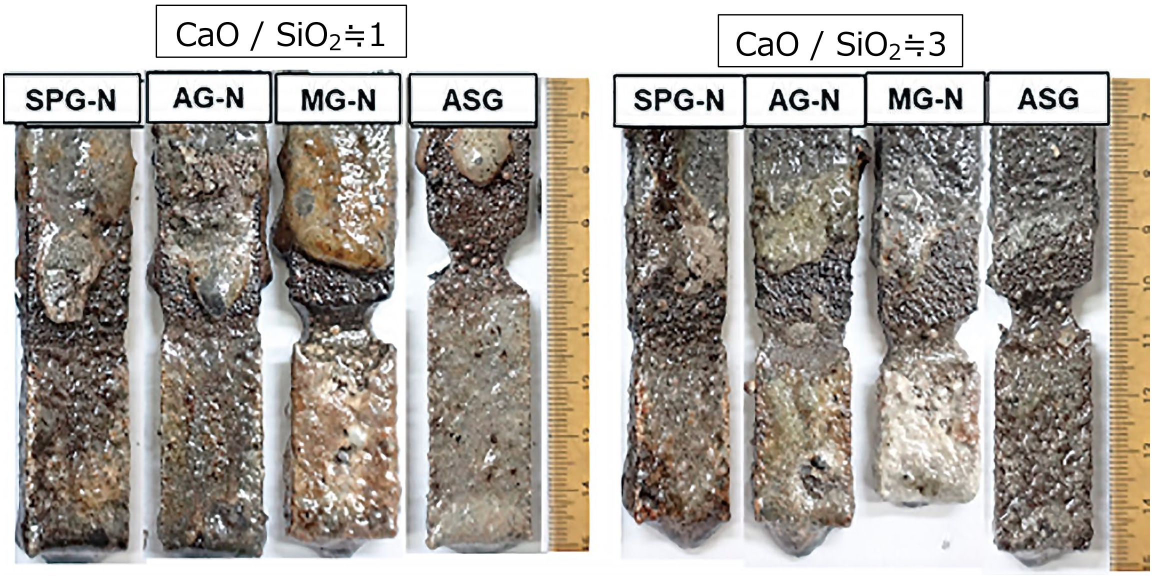

Fig. 4 Appearance of specimens after corrosion tests for CaO / SiO_2≒1 and 3, respectively.

3・3　パウダーライン用 ZG 材質の耐食性評価

パウダーライン材質の耐食性は，**Fig. 2** で示したものと同様な温度を保持された同鋼種の鋼浴面に30mm 厚さの中炭用パウダーを乗せた状態で試験片を 60min 間浸漬後，溶鋼／溶融パウダー界面における最大溶損量を測定することにより評価した。結果として，**Fig. 5** に各サンプルの試験片切断面の外観比較を示すとともに，耐熱衝撃性指向の汎用材の ZG-2 材質を 100 とした場合の溶損指数が，開発材 ZG-N では 80 となり，緻密化の効果により，耐食性指向用材質 ZG-1 の 84 よりも優れた耐食性を有すること。

3・3 Corrosion resistance evaluation of ZG materials for powder line

The corrosion resistance of the powder line material was evaluated by immersing the test material in molten steel bath for 60 min using the same molten steel with same temperature as **Fig. 2**. The test was performed by floating the mold power for medium carbon steel on the bath by the thickness of 30 mm. The maximum amount of corrosion at the molten steel / molten powder interface was measured after the test, and the corrosion resistance was evaluated by the corrosion index, when the index of the general-purpose material ZG-1 with high thermal spalling resistance was set to 100. The developed material ZG-N showed higher corrosion resistance than the ZG -2 material specified for high corrosion resistance due to densification effect, as shown in **Fig. 5**.

	ZG-N	ZG-1	ZG-2
Free C / mass%	13	13	19
ZrO_2 / mass%	82	82	77
Apparent porosity / %	13.8	17.1	16.1
Cut face appearance of specimen after corrosion test			
Corrosion rate index	80	84	100

Fig. 5 Results of corrosion test for powder line materials.

3・4　各種処理鋼に対する耐溶鋼摩耗性評価

連鋳用ノズル内孔側の環境を模擬した溶鋼流速下にて各種処理鋼に対する耐火物の溶鋼摩耗性を，**Fig. 6** に示すように，各処理鋼中で耐火物サンプルを高速回転（200 rpm）させる方法にて評価した。各処理鋼は，約 10 kg 低炭鋼を Ar 気流中に 1550 ℃で溶解した後，脱酸剤として金属 Si や Mn を添加することより準備した。Ca 処理は，鋼中酸素を 10 ppm以下に調整後，鋼浴上に CaO ／Al_2O_3 ≒ 1の溶融スラグを添加し模擬的溶鋼とした。供試材は，開発材 3 種と比較材 ASG を耐火物製撹拌治具の先端に取り付けた撹拌子を準備し，それぞれの処理鋼中で所定時間連続回転させた。溶鋼撹拌試験前後のサンプル寸法変化から損耗速度を測定し比較した。

各種溶鋼における各材質の損耗速度の計測結果を指数表示として比較して，**Fig. 7** に示している。結果として，比較材 ASG を 100 とした場合の溶損指数は，Si キルド鋼では MG-N ＞ AG-N ＞ ASG ＞ SPG-N の順に指数は低下し耐溶損性が向上した。Mn 鋼，Ca 処理鋼においては，新規開発材 3 種は，いずれも汎用材 ASG に比べ改善されている。とりわけ SPG-N 材質は，各処理鋼に対する耐溶鋼摩耗性が強いことが判明した。

3.4 Erosion/corrosion resistance evaluation against molten steels with various treatments

The wear of refractories with various treated steels was evaluated under the molten steel flow simulating the environment on the inner wall surface of the nozzle for continuous casting. The evaluation was performed as shown schematically in **Fig. 6**, where the refractory samples were rotated at a high speed (200 rpm) in molten steel with various treatments. The treated steels used for the evaluation were prepared by melting about 10 kg of low carbon steel in Ar gas flow at 1550 ℃ and then adding metallic Si or Mn as deoxidizing agent. The Ca treated steel, was also prepared by adding molten slag with CaO / Al_2O_3 ≒ 1 to the molten steel reduced the oxygen content less than 10 ppm prepared. Four test samples with three to developed materials and one comparative material ASG were attached to the tip of a refractory stirring jig as shown in **Fig. 6**, rotating continuously in each treated steel for a prescribed time. The erosion/corrosion rate calculated from the sample size change before and after the stirring test in above described three kinds of molten steel was compared.

The erosion/corrosion rate as the corrosion index of each material in various molten steels when the index of the comparison material ASG is set to 100 as shown in **Fig.** 7. The degree of erosion/corrosion lowered in the order of MG-N > AG-N > ASG > SPG-N for the Si-killed steel. For both Mn and Ca treated steels, all three newly developed materials showed superior erosion/corrosion resistance to general-purpose material ASG, in particular, the SPG-N material had quite high resistance against three kinds of the molten treated steels.

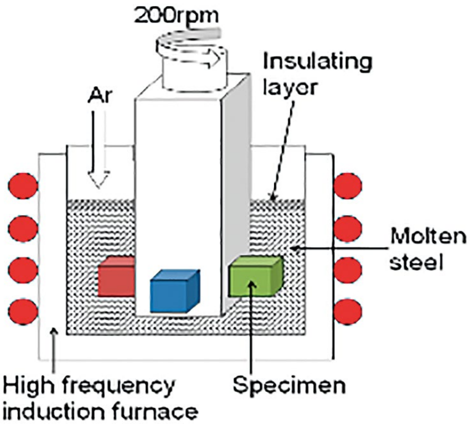

Fig. 6 Schematic illustration of erosion/corrosion test[6].

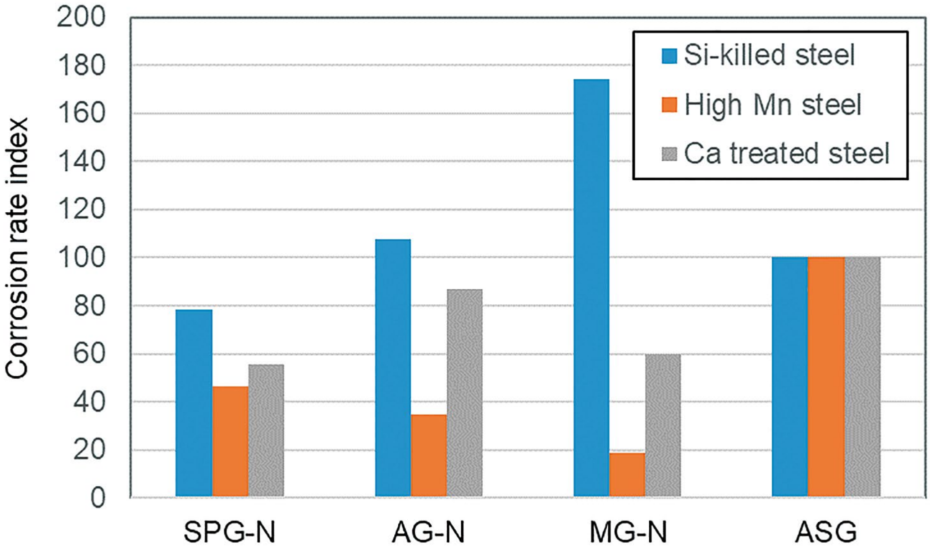

Fig. 7 Results of the erosion/corrosion test under molten steel flow.

4 実形状での構造体評価

4・1 FEM 解析による確認

材質単体の物性や耐食性のこれまでの評価を通して，開発品が無予熱材質と同等の物性を有し，予熱用材質並の耐食性も有することがわかった。そこで，実際にノズルに配置した場合の耐熱衝撃性を評価するために，まず有限要素法（FEM – Finite Element Method）による熱応力解析を行った。**Fig. 8** に示す内径 75mm，吐出孔サイズ 74mm × 80mm の浸漬ノズル（SEN）を対象とし，ノズルに配置した材質の組み合わせを **Table 4** に示す A~G の 7 種とし，1/4 モデルで計算した。ノズル全体の初期温度が 25 ℃で，内面に 1550℃の溶鋼が接し，外面が 25 ℃の空気により冷却される温度条件とし，溶鋼接触時（0 s）から，300 s 経過後までに **Fig. 8** に黒点で示した位置で発生熱応力を非定常条件で計算した。

材質組み合わせ A~D のノズルの各位置で発生する

4 Evaluation of structure in actual shape

4・1 Thermal stress analysis by FEM

We have evaluated the physical properties and corrosion resistance of the developed material, and found that they have equivalent physical property to the material specified for without preheating application, as well as equivalent corrosion resistance to that specified for preheating application. In order to evaluate the thermal spalling resistance of the nozzle composed of these materials, thermal stress analysis was performed by using the Finite Element Method (FEM). **Fig. 8** shows the illustration of the 1/4 cut model of the nozzle used in the calculations. In this study, a submerged entry nozzle (SEN) with the inner diameter of 75 mm and the outlet port size of 74 mm × 80 mm was used for the calculations, and the calculations were performed using a quarter model. The seven different combinations of refractory materials placed in the nozzle shown in **Table 4** were calculated. The temperature conditions were based on the assumption that the entire nozzle with the initial temperature of 25℃ was filled up molten steel at 1550℃ in contact with the inner surface of

熱応力の時間変化の計算結果は，Fig. 9に示すように，ノズルAの場合，溶鋼接触後30-40 sで吐出孔近傍の最大主応力がピークに達し，その後パウダーライン部や本体との材質境界部の最大主応力がピークに達することがわかる。これらの値は，15-35 MPaとなり，本体，パウダーライン部とも，通常予熱使用される材質では無予熱鋳造時に割れる可能性を示す高さであることがわかる。本体材質を通常無予熱用に用いられるASGとしたノズルBの場合，パウダーライン部や材質境界部の応力が大きく抑制されている。これは，本体材質の熱膨張率を低減させたことで，パウダーライン部内孔から押される事による引張応力が抑制されたためと理解できる。しかしながら，熱膨張率の高いパウダーライン部から作用する高い引張応力の影響を受け，吐出孔近傍の応力を十分に低減できていない。次に，本体材質は予熱用AGのままで，パウダーライン材質を開発材ZG-NとしたノズルCの場合，吐出孔コーナー部や，パウダーライン部の発生応力が抑制される一方，吐出孔柱部や，パウダーラインと本体との材質境界部の発生応力が高くなることがわかる。これらに対し，本体材質を無予熱用ASG，パウダーライン材質を開発材ZG-NとしたノズルDにおいて，吐出孔近傍や，パウダーライン部，材質境界部のいずれの発生応力も低減されている。このことから，本体材質，パウダーライン材質双方の熱膨張率を低減させることによる対策がノズルの耐熱衝撃性向上に有効であることがわかる。

パウダーライン部の材質を開発材ZG-Nとし，本体材質を開発材SPG-N, AG-N, MG-Nとした**Table 4**に示したノズルE, F, Gも含めA～Gすべてのノズルにおける，**Fig. 8**に示した各位置における最大主応力のピーク値を**Fig. 10**に示している。図から明らかなように，ノズルE, F, Gは，ノズルDと比較し同等かそれ以上に発生熱応力が低いことから，開発材SPG-N, AG-N, MG-Nは，ZG-Nと組み合わせることにより無予熱使用が可能であると考えられる。

the nozzle and cooled by air at 25℃ from the outside. The calculations were performed under unsteady conditions, with the timing of contact with the molten steel set at 0 s, and the thermal stress calculated up to the time of 300 s.

The calculated results of variation of the thermal stress with the time generated in nozzles A~D at the positions shown in **Fig. 8** as a black dot, are shown in **Fig. 9**. The results for nozzle A show that the maximum principal stress near the outlet port peaks 30-40 s after contact with the molten steel, followed by peaks at the powder line part and at its boundary with the main body material. These are too high, around 15-35 MPa, indicating a risk of cracking during non-preheating casting for materials normally used with preheating in both the body and powder line parts. Nozzle B, where the body material is ASG, which is usually used for no preheating, shows that the stresses at the powder line and the boundary parts are greatly suppressed. This can be understood because of the decreased the thermal expansion of the main body material, which suppresses the tensile stress caused by pushing from the inner hole of the powder line part. However, the stress near the outlet port is not reduced because it is affected by the tensile stress exerting from the powder line part, with high thermal expansion. In the case of nozzle C, where the material of the body remains AG for preheating and the material of the powder line is ZG-N, the stress at the corner of the outlet port and the powder line part are suppressed. But the stress at the nozzle body at the vicinity of the outlet port and at the boundary part between the powder line part and the main body are increased. On the other hand, in the case of nozzle D, where the body material is ASG (for no preheating) and the powder line material is ZG-N (developed), the stress is reduced near the outlet port, the powder line part, and the boundary. This indicates that counter measures taken by reducing the thermal expansion of both the body material and the powder line material are effective in improving thermal spalling resistance.

The peak values of the maximum principal stress at the positions shown in **Fig. 8** are shown in **Fig. 10** for combination nozzles E, F, and G, where the powder line material is the developed ZG-N and the main body materials are the developed SPG-N, AG-N, and MG-N. The results show that the stresses generated in combination nozzles E, F, and G are as low as or even lower than those in nozzle D. The developed SPG-N, AG-N, and MG-N can be used without preheating when combined with ZG-N.

Table 4 Combinations of refractory materials for the main body and power line part of the SEN used for FEM analysis

Combination	A	B	C	D	E	F	G
Main body	AG	ASG	AG	ASG	SPG-N	AG-N	MG-N
Powder line part	ZG-1	ZG-1	ZG-N	ZG-N	ZG-N	ZG-N	ZG-N

Pink: newly developed materials

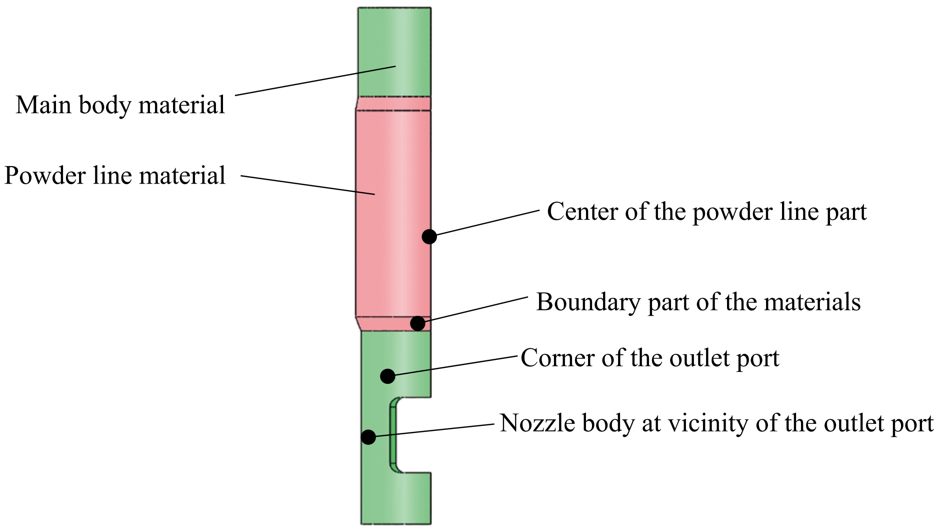

Fig. 8 **Vertical one quarter cut model of the SEN using combined materials for the parts of main body and power line, showing also four positions of thermal stress generation in the nozzle during molten steel teeming for FEM analysis.**

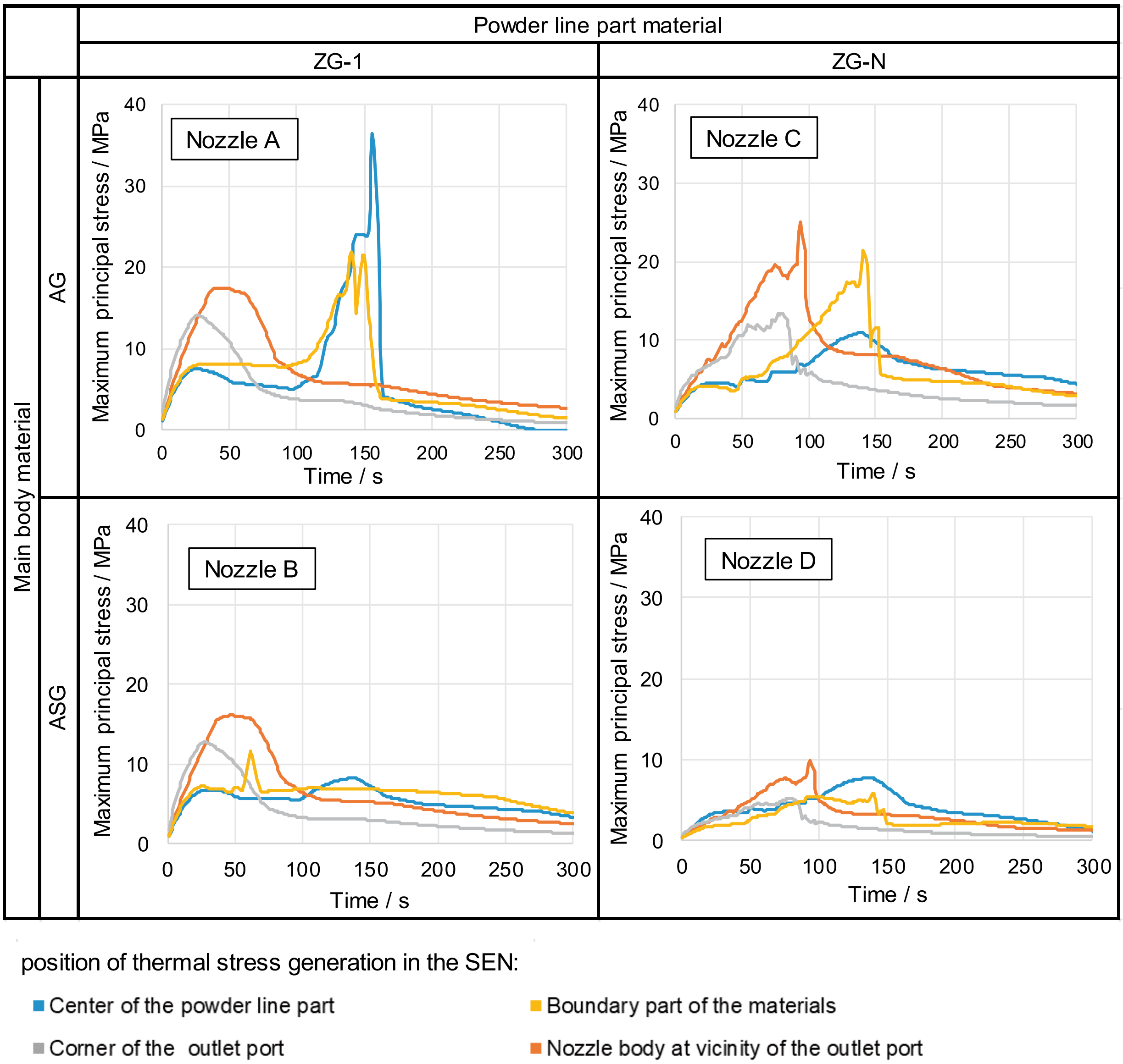

Fig. 9 **Change in the maximum principal stress generated with time at each position of the nozzles A~D.**

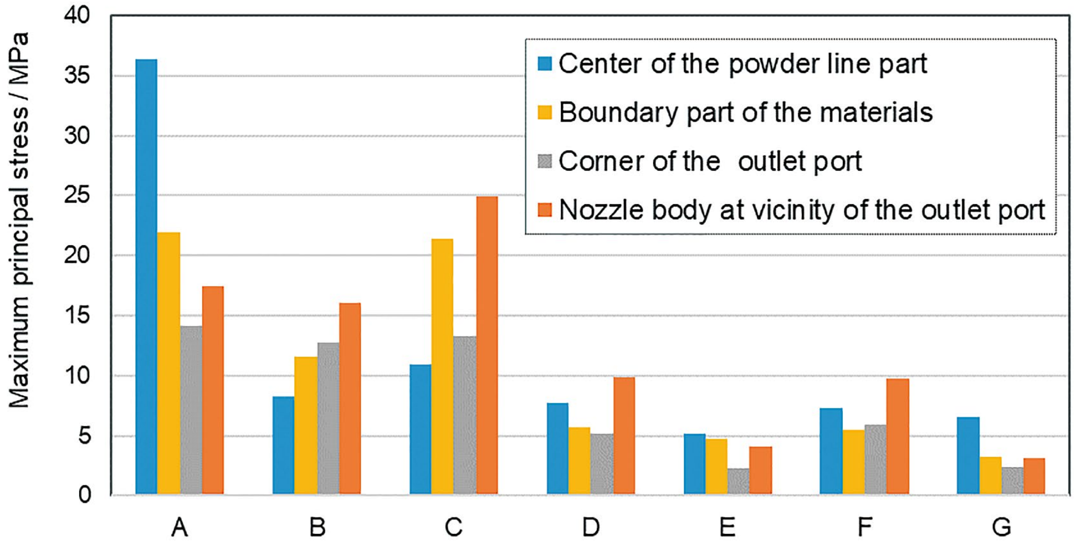

Fig. 10 Comparison of peak value of the maximum principal stress generated at each position of the nozzles A~G.

4・2　実形状ノズルでの無予熱スポーリング評価

最後に，今回開発した低膨張材質の連鋳用ノズルへの適用妥当性を確認するために，実形状ノズルにおける耐熱衝撃性を評価した。

4・2・1　ロングノズル形状での水冷評価

水中急冷法によりロングノズル形状での耐熱衝撃性評価を実施した。**Table 1** に示す開発材 SPG-N を用い，SPG-N 単層での評価用ロングノズル（下端部：外径 230 mm ／内径 160 mm- 厚み 35 mm，長さ 1390 mm，上蓋付き）を作製した。評価用ノズルは，約 1500 ℃までガス炉中で加熱され，その温度に約 30 min 間保持した後，直ちに水槽中に 3 min 間浸漬する方法でノズル外表面より急激な熱衝撃（ΔT ≒ 1500 ℃）を与えた。引き上げ後，亀裂の有無を目視観察し，亀裂がない場合は，さらにこの急冷操作をもう一度繰り返した。水冷試験後のノズルは，切断し亀裂の有無を確認した。

SPG-N 単層ノズルの耐熱衝撃性評価中の様子及び 3 サイクル後のノズル切断面写真を **Fig. 11** に示す。熱衝撃温度としてΔ T ≒ 1500 ℃を 3 サイクル与えた切断面を観察した結果，亀裂は全く見られなかった。

4.2 Evaluation of non-preheating spalling in actual shape nozzle

Finally, in order to confirm the applicability of the low-expansion material developed in the present study to the nozzle for continuous casting, the thermal shock resistance of the actual shape nozzle was evaluated.

4.2.1 Evaluation of water cooling in long nozzle shape

In order to confirm the thermal shock resistance in the long nozzle shape, the water quenching method was applied for the evaluation. Using the SPG-N material, long nozzle (bottom: outer diameter 230 mm / inner diameter 160 mm, thickness 35 mm, length 1390 mm), with top lid was produced with monolayer for the evaluation. The nozzle was heated to about 1500 ℃ in a gas furnace, kept at the temperature for about 30 min, and then immediately immersed in a water tank for 3 min to give a thermal shock (ΔT≒1500 ℃) from the outer surface of the nozzle. After pulling up from the tank, the existence of crack was checked visually in the sample nozzle, and if there was no crack, the quenching operation was repeated again. The nozzle after the water cooling test was finally cut and the existence of the crack was checked precisely.

Figure 11 shows a view of the thermal shock resistance evaluation test for the SPG-N monolayer nozzle and a cutaway view of the nozzle after three cycles of thermal shock test. No crack was observed on the cut surface subjected to 3 cycles of ΔT≒1500 ℃ in the long nozzle made of developed material SPG-N.

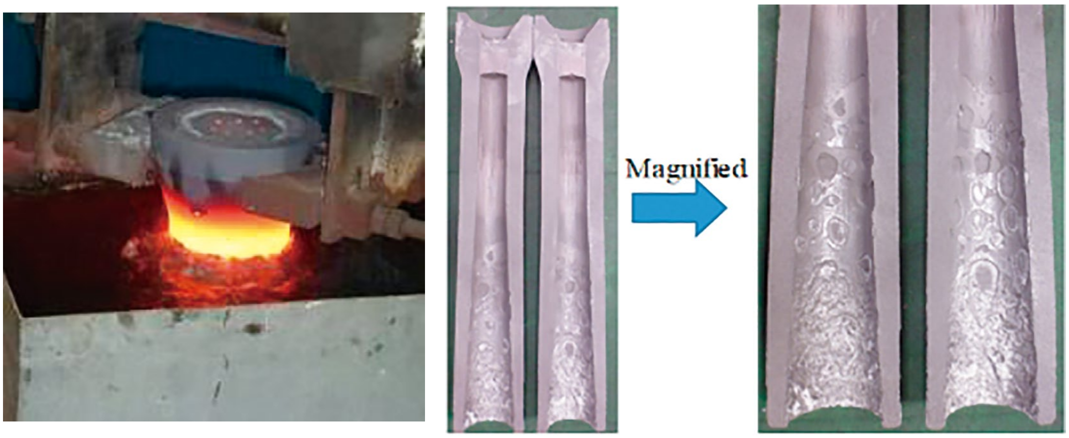

Fig. 11 Appearance of thermal spalling test and resultant half-cut test sample of SPG-N with sound state.

4・2・2　浸漬ノズル形状での注湯テスト評価

浸漬ノズル形状での無予熱条件での耐割れ性を確認するため，注湯テストによる耐熱衝撃性評価を実施した。**Table 1, 2** に示すように，開発材 SPG-N を本体材質として，開発材 ZG-N をパウダーライン材質として配置した評価用ノズル（外径 130 mm，内径 70 mm，長さ 850 mm，底蓋付き）を作製した。ノズルは焼成品のため吸湿の恐れがあるため，試験前に乾燥処理を行い，1600 ℃の溶銑を約 300 kg 注湯した。試験のイメージと試験後ノズルの外観写真及び浸漬部切断面写真を **Fig. 12** に示す。熱衝撃温度としてΔＴ≒1550℃を与えた結果，ノズルに亀裂は全く見られなかった。

4.2.2 Molten steel teeming test in submerged entry nozzle (SEN) shape

The thermal shock resistance under the non-preheating condition in the SEN, was also evaluated in the material combination of the developed SPG-N for the main body and the developed ZG-N material for the powder line parts, respectively. The nozzle (in size of outer diameter 130 mm, inner diameter 70 mm, length 850 mm), with bottom lid was dried before the test, in order to eliminate moisture possibly absorbing in fired nozzle body, then about 300 kg of 1600 ℃ molten pig iron was poured into the SEN as schematically shown in **Fig. 12 (a)**. General view of the testing apparatus, appearance of the SEN after the test and cut cross section of the immersed part are also showing **Fig. 12 (b), (c) and (d)** respectively. No cracking was occurred in the tested SEN even for thermal shock corresponding to ΔT≒1500 ℃ under the non-preheating condition.

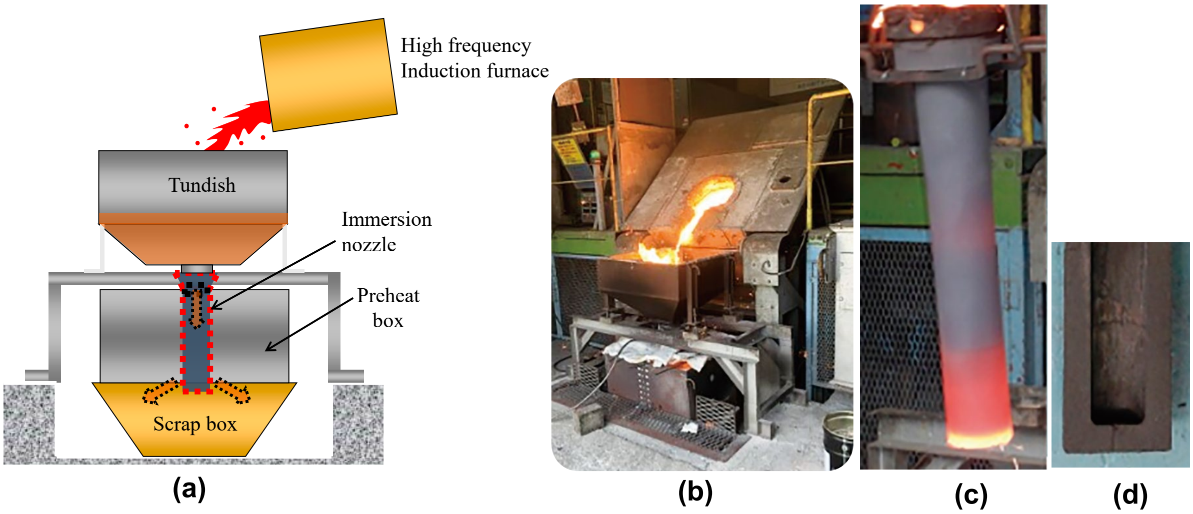

Fig. 12 Illustration and appearance of molten pig iron teeming test ((a) and (b)) for sample with SPG-N and ZG-N, showing also appearance of nozzle after the test (c) and cut cross section in the vicinity of the outlet port (d) of the nozzle.

５　まとめ

化学成分の調整に依らず，耐火物の気孔形態の制御による低膨張化技術を適用して，易溶損成分（炭素やシリカ）を最少にすることにより，開発した低膨張で緻密質なアルミナ－グラファイト（AG-N），マグネシア－グラファイト（MG-N），スピネル－グラファイト（SPG-N），ジルコニア－グラファイト（ZG-N）４種の材質は，優れた耐熱衝撃性を有し，ノズル形状によっては，予熱をほとんどすることなく使用できることを示した。また，近年増加している，Ca 処理鋼などの侵食性の強い鋼種に対する高耐食化ニーズへの対応も期待できる。さらに，鋳造用ノズルの無予熱化は，予熱用燃料コストの削減や CO_2 ガス発生の抑制を通して，カーボンニュートラルの実現に向けた製鉄所の環境負荷低減技術の１つと考えられる。

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5 Summary

Thermal expansion property of the refractories could be improved through controlling the pore morphology and minimizing the corrosion-facilitating components such as carbon and silica. Using above described method, four materials of alumina-graphite (AG-N), magnesia-graphite (MG-N), spinel-graphite (SPG-N), and zirconia-graphite (ZG-N) with low thermal expansion and high density were newly developed. Since these materials have excellent thermal shock resistance, they can be used as nozzle with almost no preheating depending on the shape. They are also expected as the high corrosion resistant refractories for processing the steels with strong corrosiveness such as Ca treated steel increasing recently. Free from preheating in casting nozzles, in addition, leads to reduction in both fuel cost for heating and generation of CO_2 gas, with contributing possibly as one of the environmental loading reduction technologies in the steel industry for realization of carbon neutrality in future.

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