高温焼成 SN プレートへの Al_4O_4C 原料の添加効果

Application effect of Al_4O_4C raw material for high temperature firing type SN plate

西田　心*，高見行平**，赤峰経一郎***，清水公一****，後藤　潔*****
Shin NISHIDA*, Kohei TAKAMI**, Keiichiro AKAMINE***,
Koichi SHIMIZU**** and Kiyoshi GOTO*****

要　旨

高温焼成タイプの Al_2O_3-C 質スライディングノズルプレート材質に Al_4O_4C 原料を適用し，比較として，アルミナ骨材原料のみを適用した粒度構成が同じ材質を基準として，Al_2O_3-ZrO_2 系原料２種（AZ1，AZ2）と ZrO_2-mullite 系原料２種（ZM1，ZM2）を，それぞれ添加量を変えて適用した材質も併せて特性を評価した。Al_4O_4C 原料を 24 mass% まで添加すると，基準材質と比較して，耐熱衝撃性は向上し，同等以上の耐食性を示した。一方，AZ1 及び ZM 系原料２種（ZM1，ZM2）は，添加量が多いほど，耐熱衝撃性が向上するが，耐食性は低下し，特にその傾向は ZM 系原料で強く見られた。AZ2 原料では，緻密化や高強度化の傾向が見られ，耐熱衝撃性は低下したが，耐食性の低下は他の ZrO_2 含有原料と比較して小さかった。

Abstract

Al_4O_4C raw material was applied to the material of Al_2O_3-C system sliding nozzle plate of high-temperature firing type. As comparison, the material applied to only alumina aggregate with the same particle size composition as a base, the materials with 2 kinds of Al_2O_3-ZrO_2 (AZ) system raw materials and 2 kinds of ZrO_2-mullite (ZM) system raw materials applied were selected. The properties of the materials with additions of raw material aggregate with three levels were investigated. When the Al_4O_4C raw material were added up to 24 mass%, the thermal shock resistance was improved in comparison with the base material, and the corrosion resistance was almost equivalent or better than the base material. On the other hand, AZ with low ZrO_2 content and 2 ZM system raw materials had increased thermal shock resistance with increasing amount of raw material addition, but the corrosion resistance was lowered, in particular, the tendency was seen in ZM raw materials intensively. The addition of the AZ with high ZrO_2 content is rather effective for densification with increasing the modulus of rupture but the thermal shock resistance, the deterioration degree of corrosion resistance was suppressed in comparison to the other ZrO_2 system raw materials.

1　緒言

スライディングノズル（以下 SN）プレートは，連続鋳造プロセスにおいて取鍋及びタンディッシュで溶鋼の流量を制御する SN 装置に組み込まれる耐火物である。２枚もしくは３枚一組で使用され，それらを摺動させることによりプレートに開けられたノズル孔の開度を調節し，溶鋼の流量を制御する

1 Introduction

Sliding nozzle (henceforth, SN) plates are refractories incorporated into the SN devices that control the flow rate of molten steel in ladles and tundishes in continuous casting process. Two or three plates are used as a set, and they are slid each other to adjust the opening of nozzle hole in the plates and to control the flow rate of molten steel. Generally, the SN plates made of Al_2O_3-ZrO_2-C system material

＊　技術研究所 製品プロセス研究センター　Product R&D Center, Technical Research Institute
＊＊　技術研究所 製品プロセス研究センター アシスタントマネージャー　Assistant Manager, Product R&D Center, Technical Research Institute
＊＊＊　技術研究所 製品プロセス研究センター マネージャー　Manager, Product R&D Center, Technical Research Institute
＊＊＊＊　技術研究所 製品プロセス研究センター センター長　Center Manager, Product R&D Center, Technical Research Institute
＊＊＊＊＊　フェロー 技術研究所 所長　Fellow, General Manager, Technical Research Institute

ために用いられる。一般に取鍋では Al_2O_3-ZrO_2-C 系材質かつ高温焼成タイプのSNプレートが適用されている[1,2)]。ZrO_2 含有原料は，耐熱衝撃性や耐食性の向上に有効であると考えられており，主に Al_2O_3-ZrO_2（以下AZ）系原料，ZrO_2-mullite（以下ZM）系原料などの骨材原料が使用されている。

Al_4O_4C 原料（以下AOC）については，その特性と，低温焼成タイプのSNプレート材質への適用効果ならびに，実機使用結果について赤峰らが報告[3,4)]したように低熱膨張率，低かさ密度という特徴を持ち，耐熱衝撃性の改善や軽量化などの効果が期待できる。また，高温焼成タイプのSNプレート材質にAOC原料を適用した場合，ZrO_2 含有原料を適用した材質と比較して，低かさ密度で，耐熱衝撃性及び耐食性も同等あるいはそれ以上という結果[5)]を得ている。

本報告では，高温焼成タイプのSNプレート材質をベースに，AOC原料と，ZrO_2 含有原料として新たに緻密タイプの低熱膨張ZM系原料[6)]を加え，AZ系原料2種，ZM系原料2種の合計5種の原料系において，それらの添加効果を比較した。また，今回，これらの骨材原料添加量を同一とし，サンプルの粒度構成を出来るだけ一定とするために骨材原料の粒度を調整して添加し，材質特性に及ぼす各骨材原料の添加効果を比較検討した。

2　実験方法

2・1　サンプル調製

高温焼成タイプのSNプレートの骨材原料を，すべて電融アルミナに置き換えた材質Aをベースとして，ZrO_2 含有原料及びAOC原料の添加量を変えて調製したB～Pの15材質（**表1**参照）において，特性を評価した。なお，各材質は，原料のかさ密度を考慮して，粒度構成が同一となるように調整した。ZrO_2 含有原料は，組織及び ZrO_2 量が異なる2種類のAZ系原料（AZ1,AZ2）と2種類のZM系原料（ZM1,ZM2）を用いた。これらの原料を含む配合を混練，所定の条件で成形した後，非酸化雰囲気下，1000 ℃以上の高温で焼成し評価

with high temperature fired type are applied in the ladle.[1, 2)] The ZrO_2 containing raw materials are considered to be effective for improving both thermal shock resistance and corrosion resistance, and aggregate raw materials of Al_2O_3-ZrO_2 (henceforth, AZ) and ZrO_2-mullite (henceforth, ZM) systems have been used. Al_4O_4C raw material (henceforth, AOC) is characterized by low thermal expansion coefficient with low bulk density and is applied to low temperature fired SN plates. As confirmed in the application to actual production line by Akamine et al. [3, 4)], the application of the material is expected to improve the thermal shock resistance and to lighten the weight of the plate. In addition, even if the material is applied to the high-temperature firing type, the properties of the SN plate material are equivalent or even superior in both to thermal shock and corrosion resistances[5)] with low bulk density that applied the ZrO_2 containing raw material. at, are also obtained as equal or higher.

In this report, on the basis of the SN plate material with the high temperature firing type, AOC raw material and adding a new dense type low thermal expansion ZM raw material[6)] as ZrO_2 containing raw material, the application effect was compared in the 5 kinds raw material system of in total, including 2 kinds of AZ and 2 kinds of ZM raw materials. In addition, in order to clarify the application effect of each aggregate raw material on the material characteristics, the particle size composition of each sample made almost equivalent in the sample with the same amount of aggregate raw materials.

2 Experimental methods

2･1 Preparation of sample

On a sample of the base material A prepared by replacing all the aggregate raw materials of the high-temperature firing type SN plate material to the electrofused alumina and the other 15 samples (see **Table 1**) of B to P prepared by changing the amounts of ZrO_2 containing system aggregate raw materials and AOC aggregate raw material, various properties were investigated. Each sample was prepared to have almost equivalent particle size composition with consideration of the difference in bulk density of the aggregate raw materials. ZrO_2 containing aggregate raw materials, including 2 types of AZ raw materials (AZ1, AZ2) and 2 types of ZM raw materials (ZM1, ZM2) which differ in microstructure and ZrO_2 content were used. After kneading the mixtures containing each raw material and molding under a predetermined condition, the samples were fabricated

Table 1 Amount of aggregate raw material and composition of all the samples tested

		A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P
	Sample	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P
Raw material system / mass%	AZ1	-	12	24	36	-	-	-	-	-	-	-	-	-	-	-	-
	AZ2	-	-	-	-	12	24	36	-	-	-	-	-	-	-	-	-
	ZM1	-	-	-	-	-	-	-	12	24	36	-	-	-	-	-	-
	ZM2	-	-	-	-	-	-	-	-	-	-	12	24	36	-	-	-
	AOC	-	-	-	-	-	-	-	-	-	-	-	-	-	12	24	36
Composition / mass%	Al_2O_3	93.0	90.0	87.0	84.0	88.2	83.4	78.6	86.6	80.3	73.9	86.5	80.0	73.6	92.4	91.8	91.2
	ZrO_2	-	3.0	6.0	9.0	4.8	9.6	14.4	4.2	8.4	12.6	4.7	9.4	14.0	-	-	-
	SiO_2	-	-	-	-	-	-	-	2.2	4.3	6.5	1.8	3.6	5.4	-	-	-
	T.C. (F.C.)	3.7	3.7	3.7	3.7	3.7	3.7	3.7	3.7	3.7	3.7	3.7	3.7	3.7	4.3	4.9	5.5
	Others	3.3	3.3	3.3	3.3	3.3	3.3	3.3	3.3	3.3	3.3	3.3	3.3	3.3	3.3	3.3	3.3

サンプルを作製した。

2・2 供試骨材原料の特性

表 2 に適用した骨材原料種の特性を示す。AZ1 は ZrO_2 を 25 mass% 含有し，コランダムと少量の正方晶 ZrO_2 を含む未安定化 ZrO_2 から構成され，見掛気孔率が約 2.4%と緻密な組織を有し，AZ2 は ZrO_2 を 40 mass% と AZ 1よりも多く含有し，見掛気孔率も 4.6%と高く AZ 1よりも粗い組織となっている。ZM1 は主にムライトと 37 mass% の未安定 ZrO_2 とで構成され，ZM2 もムライトと未安定 ZrO_2 で主に構成されているが，少量の正方晶 ZrO_2 を含み，見掛気孔率が 1.7%と低い密な組織を有している。AOC は Al_4O_4C と少量の Al_2O_3 を含む原料である。

by firing at temperatures higher than 1000 ℃ in unoxidizing atmosphere.

2･2 Properties of aggregate raw materials

Composition and some properties of aggregate raw material systems are summarized in **Table 2**. AZ1 contains 25 mass% ZrO_2, which consists of corundum and unstabilized ZrO_2 containing a small amount of tetragonal ZrO_2, and has a dense structure with apparent porosity of about 2.4%. AZ2 has higher ZrO_2 content than AZ1 with 40 mass% and apparent porosity of about 4.6%, which has coarser structure than the AZ1. ZM1 is mainly composed of mullite and 37 mass% of unstabilized ZrO_2. ZM2 is also mainly composed of the mullite and the unstable ZrO_2, but it contains a small amount of tetragonal ZrO_2 and has a dense structure with about 1.7 % apparent porosity. AOC is a raw material containing crystal of crystal of Al_4O_4C compound and a small amount of Al_2O_3.

Table 2 Composition and some properties of aggregate raw material system

	Raw material system	Al_2O_3	Al_2O_3-ZrO_2		Mullite-ZrO_2		Al_4O_4C-Al_2O_3
	Notation	Fused Al_2O_3	AZ1	AZ2	ZM1	ZM2	AOC
Bulk density	/ $g\cdot cm^{-3}$	3.68	4.23	4.42	3.60	3.70	2.79
Apparent porosity	/ %	6.2	2.4	4.6	3.1	1.7	4.7
Composition / mass%	Al_2O_3	99	74	59	45	45	95.1
	ZrO_2	−	25	40	37	38	−
	SiO_2	−	−	−	18	16	−
	T.C.	−	−	−	−	−	4.6
Mineral phase*	m-ZrO_2 (Baddeleyite)	−	○	○	○	○	−
	t-ZrO_2	−	△	−	−	△	−
	Mullite	−	−	−	○	○	−
	Corundum	◎	◎	◎	−	−	○
	Al_4O_4C	−	−	−	−	−	◎

* Identified by X-ray diffraction with Rietveld analysis

2・3　耐熱衝撃性評価試験

前述のように作製したサンプルから，40 × 40 × 160 mm の角柱形状試験片を切り出した。試験は，高周波誘導加熱炉を用いて 1600 ℃の溶銑に試験片を 3 min 間浸漬した後，30 s 間水冷し，これを 3 回繰り返した。試験後の外観及び切断面における亀裂の程度から，耐熱衝撃性を評価した。

2・4 耐食性評価試験

試験は，試験片を内張りした高周波誘導加熱炉内に，銑鉄と C/A（CaO/Al_2O_3）2 の合成スラグの混合融体を 1600 ℃で 3 h 保持することにより実施し，耐 CaO 性を評価した。試験後のサンプルの断面から減寸量を計測して，溶損速度を求めた。評価試験の組み合わせを**表 3** に示す。バッチ間の比較のため，基準となるサンプル A については全セットで試験した。

3　結果と考察

3・1　骨材原料の微視組織と熱膨張率

図 1 に各骨材原料のミクロ組織写真を示す。AZ1 は径 50 μm 程度の初晶のコランダムと，コランダムとバデライトの共晶部より構成され，比較的空隙が少なく緻密な組織を持つ。これに対し AZ2 はコランダムとバデライトの結晶より構成され，初晶コランダムが約 100 μm 径，バデライトが約 10 μm 径と大きく，結晶粒界部分に空隙を多く含む低密度組織である。AZ1 は小さな初晶コランダムと緻密な共晶組織を持つ高弾性な原料である。このような AZ 系原料を骨材として適用した場合，耐

2·3 Examination of thermal shock resistivity

Prismatic shaped specimens of 40×40×160 mm were cut out from the samples prepared as previously described. Each sample was immersed in hot metal heated in high frequency induction furnace at 1600 ℃ for 3 min, followed by water cooling for 30 s, and the heat cycle was repeated 3 times. Checking the appearance of specimen and the degree of cracking (number of through cracks) on the cut surface of the specimen after the test, the thermal shock resisting was determined.

2·4 Examination of corrosion property

The test apparatus for corrosion test is composed of a crucible lined the inner wall by test specimens. The crucible has a heating system with high frequency induction furnace. Corrosion test was carried out in the crucible by holding a mixed melt of pig iron and synthesized slag of C/A (CaO/ Al_2O_3)2 for 3 h at 1600 ℃ and actually corrosion resistance to CaO was checked. Corrosion rate was determined by measuring the amount of reduction in size from the cross section of the specimen after the test. **Table 3** shows the combination of corrosion tests. For batch-to-batch comparisons, the reference base material sample A was tested in all sets.

3 Results and Discussion

3·1 Microstructure and thermal expansion coefficient of aggregate raw materials

Figure 1 shows the microstructure of each aggregate raw material. AZ1 is composed of corundum of primary crystals of about 50 μm in diameter and eutectic crystals of corundum and baddeleyite, and has a dense structure with relatively few voids. In contrast, AZ2 is composed of corundum and baddeleyite crystals. The primary corundum crystals are about 100 μm in diameter, and the baddeleyite crystals are about 10 μm in diameter, and they have low density structure containing many voids in the grain boundaries area. AZ1 is a highly elastic raw material with small primary corundum grain and dense eutectic structure. When a crack

Table 3 Combination of samples for corrosion tests of 1st to 3rd set

Sample	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P
Raw material system	-	AZ1			AZ2			ZM1			ZM2			AOC		
Amount / mass%	0	12	24	36	12	24	36	12	24	36	12	24	36	12	24	36
1st set	●	●			●			●			●			●		
2nd set	●		●			●			●			●			●	
3rd set	●			●			●			●			●			●

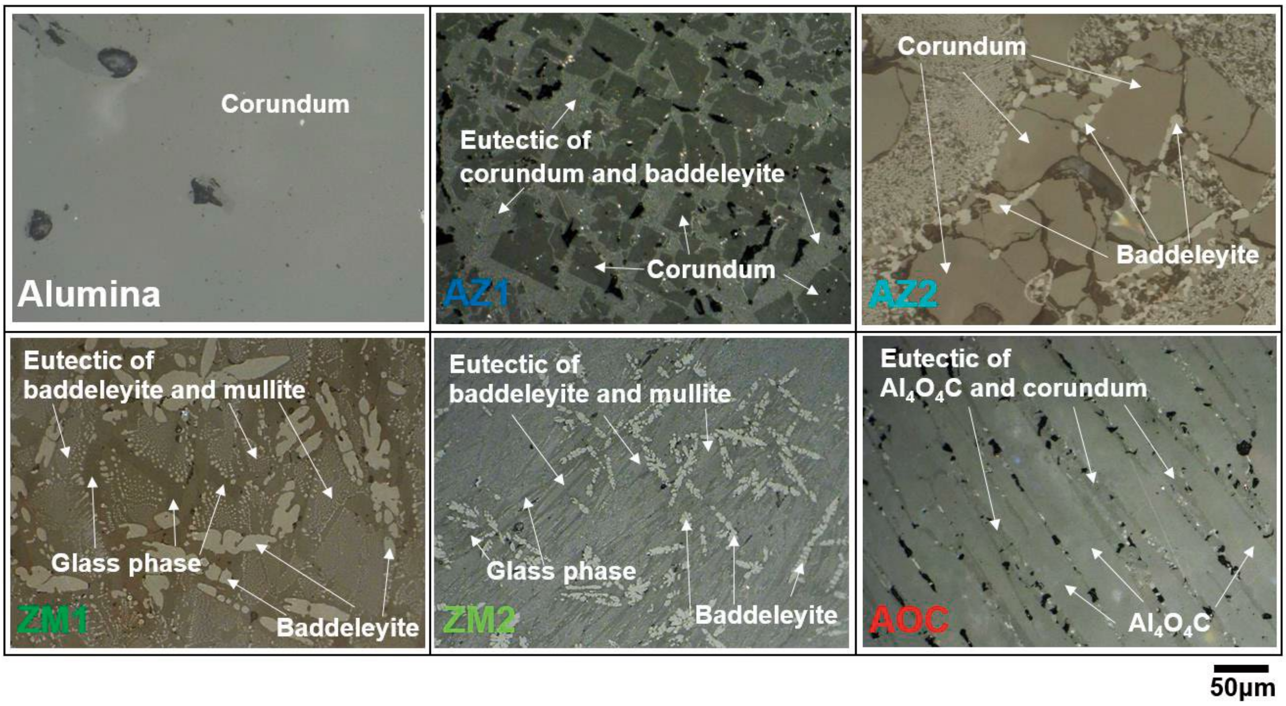

Fig. 1 Microstructure indicating the identified phases in each aggregate raw material.

火物中に亀裂が発生し骨材に到達した時，骨材を回避して亀裂が屈曲して耐火物内を進展する場合，あるいは亀裂が骨材内を進展する場合もコランダム粒を回避しながら屈曲して進展する。いずれにしても亀裂の直線的な進展よりも多くの破壊エネルギーが消費され、亀裂の抑制につながると報告[7]されている。一方，井上らは，単斜晶系の ZrO_2 含有量が多い骨材原料を適用すると，骨材原料自体の相転移に伴うヒステリシスや残存膨張が大きくなることによって，耐火物内にマイクロクラックを生じ，弾性率を低減して，耐熱衝撃性が改善されると報告[8]している。ZM1 は長径 100-200 μm 程度の初晶バデライトと微細なバデライト - ムライト共晶，それらの間を埋めるようなガラス相が観察される。ZM2 は，長径 20-30 μm 程度の微細な初晶バデライトと，さらに微細なバデライト - ムライト共晶，そしてガラス相で構成されており，組織に空隙が少なく，ZM1 と比較して非常に緻密である。AOC は径数百 μm 程度の初晶 Al_4O_4C と，Al_4O_4C とコランダムの共晶部から構成されている。

各骨材原料の TMA（Thermomechanical analyzer）による熱膨張率の測定結果を**図 2** に示

initiates in the refractories containing an aggregate raw material like AZ and propagates to the aggregate, the crack is often deflected the path in the refractories by the obstruction of the aggregate, or even if the crack propagates into the aggregate, it is forced to deflect the path by the obstruction of corundum grains in the aggregate. In any cases, a considerable fracture energy dissipation is required compared to the case of the linear propagation of the cracks, leading to the suppression of cracking.[7]

On the other hand, Inoue et al. have reported that when the ZrO_2 based aggregate raw material containing high monoclinic ZrO_2 crystal is applied, increased hysteresis and residual expansion due to the phase transition in the raw material itself, results in the occurrence of the microcracks inside the refractories thereby reducing the modulus of elasticity and improving the thermal shock resistance.[8] ZM1 contains primary baddeleyite having a major axis of about 100-200 μm and fine baddeleyite-mullite eutectic crystals, the glass phase is observed to fill between those crystals. ZM2 is composed of fine primary baddeleyite with the major axis of about 20-30 μm and further fine baddeleyite-mullite eutectic, glass phase, with less voids in the much denser structure compared to the ZM1. AOC is composed of Al_4O_4C of primary crystals of about a few hundred micrometers in diameter and the eutectic of the Al_4O_4C and the corundum.

The thermal expansion coefficient measured

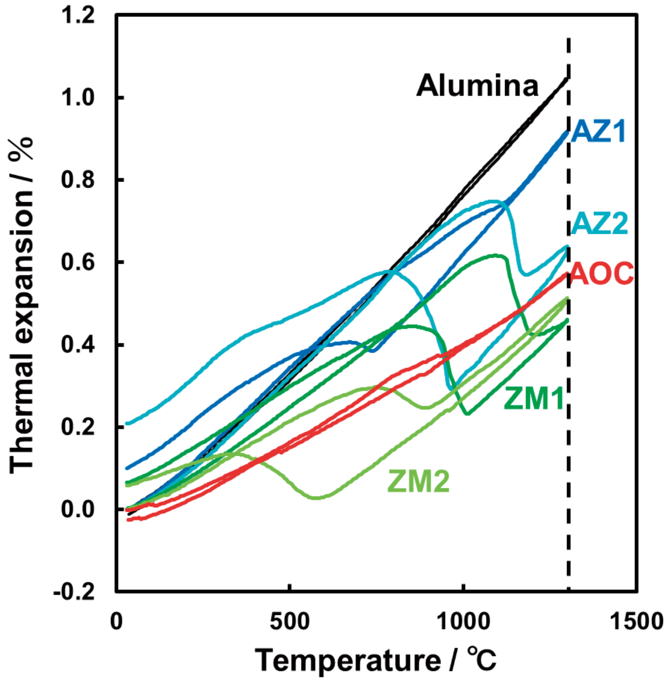

Fig. 2 Thermal expansion properties of the aggregate raw materials.

す。アルミナ及びAOCは直線的な熱膨張挙動を示すのに対して，ZrO_2含有原料は，いずれもZrO_2の相転移に伴う膨張のヒステリシスを示す。相転移に伴う体積変化は，骨材原料中のバデライトの量と粒の大きさに依存する[9]と考えられる。AZ1とAZ2を比較すると，バデライト量が少なく，緻密で微細な結晶から構成されるAZ1の方が，AZ2よりも相転移に伴う体積変化や残存膨張が小さい。また，ZM1とZM2を比較すると，初晶バデライトが小さく，緻密で微細なZM2の方が相転移に伴う体積変化が小さく，残存膨張も小さい。1300 ℃での熱膨張率を比較すると，ZM1 ≦ ZM2 ＜ AOC ＜ AZ2 ＜ AZ1 ＜アルミナ の順で高くなっている。AOCはアルミナの約半分程度の熱膨張率で，直線的な挙動を示す。

3・2 SNプレート材質の特性に及ぼす骨材原料添加量の影響

3・2・1 熱膨張率，かさ密度，見掛気孔率，曲げ強さ及び弾性率

各材質の焼成体の線変化率を各骨材原料ごとに**図3**に示す。ZrO_2含有原料は，全般的に添加量が多いほど，線膨張が大きくなる傾向が見られた。

by TMA (Thermomechanical analyzer) of the aggregate raw materials is shown in **Fig. 2**. Alumina and AOC show linear thermal expansion behavior, whereas ZrO_2 containing raw materials have a hysteresis of expansion due to the ZrO_2 phase transitions. The volume change with the phase transition seemed to depend on the amount of baddeleyite in the aggregate raw material and the size of baddeleyite crystals.[9] When AZ1 and AZ2 are compared, the volume change and residual expansion due to the phase transition are smaller in the AZ1 composed of dense and fine crystals compared to the AZ2. Further, when comparing ZM1 and ZM2, the volume change and the residual expansion due to the phase transition in the dense and fine ZM2 with fine primary baddeleyite crystals is small compared to the ZM1. The thermal expansion coefficient at 1300 ℃ became lower in the order of ZM1≦ZM2 ＜AOC＜AZ2＜AZ1 ＜alumina. The AOC exhibits a linear expansion behavior with a thermal expansion coefficient of about half that of the alumina.

3･2 Effect of amount of aggregate raw materials on the properties of the SN plate materials

3･2･1 Thermal expansion coefficient, bulk density, apparent porosity, modulus of rupture and modulus of elasticity

In the fired body of each sample, the dependence of amount of aggregate raw material on the permanent linear change of the material with each raw material are shown in **Fig. 3** in reference to

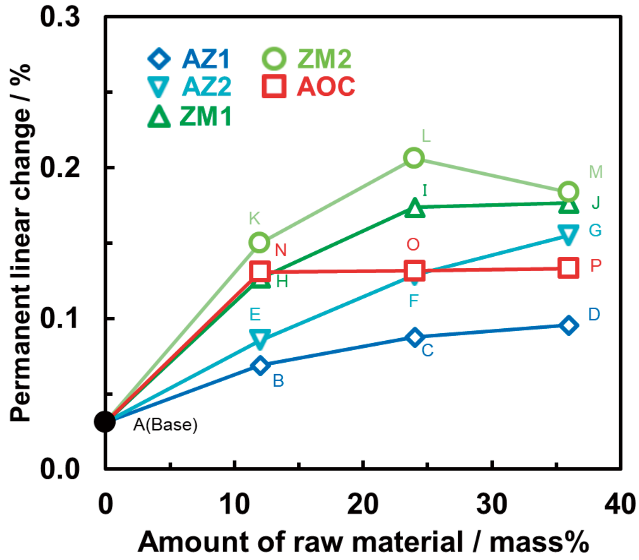

Fig. 3 Dependence of amount of aggregate raw material on the permanent linear change of material with each raw material system in reference to the base material (sample A).

なかでも，ZM2 は 24 mass% 添加で最大の線膨張を示したが，AZ1 系では添加に伴う線膨張変化が最も小さく，骨材原料自体の，相転移に伴う体積変化や残存膨張などの熱膨張挙動が及ぼす影響の大きさを示していた。AOC 系は，12 mass% までの添加で増加するものの，それ以上の添加ではほぼ一定となる特異な挙動を示した。これは，焼成時に，AOC 骨材の焼結が進行し骨材周囲に微小な空隙を生じることによるためであると推測された。

図 4 (a) 及び **(b)** に各サンプルのかさ密度及び見掛気孔率を骨材原料添加量に対してそれぞれプロットしたグラフを示す。かさ密度は，骨材原料種のかさ密度に依存した傾向がみられ，アルミナ原料よりも高かさ密度の原料を添加すると，高かさ密度となり，低かさ密度の原料では低かさ密度となった。一方で，見掛気孔率は，必ずしも骨材原料自体の気孔率の影響を受けず，AZ1 を除く各原料とも 12 mass% 添加で最小の見掛気孔率となり，それ以上の添加で，添加量の増加とともに見掛気孔率が高くなった。これは，12 mass% あるいはそれ以下の添加では，原料自体の気孔率の影響を受けるが，24 mass% 以上では，焼成による骨材原料の熱膨張の影響を強く受け見掛気孔率の増大が起こったものと考えられた。特に ZrO_2 含有原料

the base material (Sample A). The permanent linear change of the material with the ZrO_2 aggregate raw materials tended to increase with increasing amounts of aggregate raw materials, being affected largely by the thermal expansion behavior with the volume change and residual expansion due to phase transition of the aggregate raw materials. Among them, ZM2 showed the largest permanent linear change with the addition of 24 mass%, while the change was the smallest in the materials with the AZ1 system. Permanent linear change of materials with AOC showed a peculiar behavior, which increased with addition up to 12 mass%, but became almost constant with further addition. It was presumed that suppression of the expansion occurred during firing of the materials with the AOC aggregate by contracting action of them. Although the sintering of the AOC aggregates is accompanied with the formation of the small voids around them, the voids shrink and disappeared during the course of firing.

Figure 4 (a) and **(b)** shows graphs obtained by plotting the bulk density and apparent porosity of each sample against the amount of the aggregate raw material, respectively. The bulk density tended to depend on that of the raw material species, and when the raw material having the higher bulk density than that of alumina raw material was added, it became high, and in raw material having a low bulk density, it became low. On the other hand, the apparent porosity is not necessarily affected by that of the raw materials themselves. The lowest apparent porosity at 12 mass% addition of the respective raw materials, the addition of more than that, the apparent porosity increased with increasing the amount of the aggregate raw materials except for AZ1. It is considered that

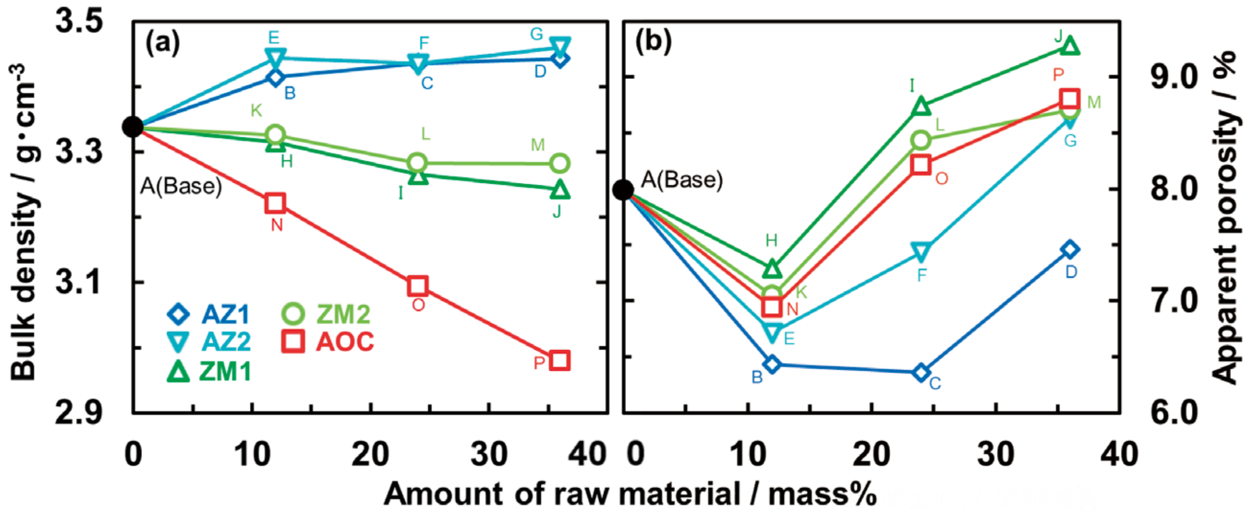

Fig. 4 Dependence of amount of aggregate raw material on bulk density (a) and apparent porosity (b) of material with addition of each raw material system.

では，その添加量が多いほど膨張が大きくなり，特に線膨張が大きいZM1とZM2添加サンプルの見掛気孔率が最も高くなった。一方で，線膨張が最も小さかったAZ1添加サンプルが最も低見掛気孔率となっている。各骨材原料ごとに見掛気孔率を比較すると，AZ1＜AZ2＜AOC＜ZM2＜ZM1の順で高くなった。

図5に各サンプルの常温曲げ強さと弾性率の関係をそれぞれの骨材原料種ごとにグループとして示す。AZ1添加サンプルは，電融アルミナ骨材ベースのサンプルAと比較して，高強度，高弾性率側に位置しており，電融アルミナと比較してAZ1の組織が緻密で高強度，高剛性になることが示された。一方ZM系原料添加では，サンプルAと比較して，低強度，低弾性率側に位置し，弾性率低減に有効であることを示している。AZ2とAOCはAZ1及びZMの中間的な位置づけとなるが，サンプルAと比較するとやや低弾性率側に位置した。各サンプルの強度及び弾性率は，各骨材原料固有の強度等の機械的特性及び熱膨張等の熱的性質によってもたらされる組織の緻密さなどに依存して決定されるものと考えられた。

although the porosity is affected by that of the raw materials themselves for the addition of 12 mass% or less, the porosity is strongly affected by the thermal expansion during the firing of the aggregate raw materials for the addition of 24 mass% or more. Especially, ZrO_2 containing aggregate raw material has a tendency that the linear expansion increases as the addition amount increases, and in particular, the apparent porosity of the materials with both ZM1 and ZM2 which have large permanent linear change became the highest and the next, respectively. On the other hand, the lowest apparent porosity was obtained in the materials with the AZ1 which has the smallest linear expansion. The apparent porosity of the materials added the aggregate raw materials tended to become higher in the order of AZ1＜AZ2＜AOC＜ZM2＜ZM1.

The relation between the modulus of rupture and modulus of elasticity of each material as a group for each aggregate species is shown in **Fig. 5**. It was shown that the group of AZ1 added was located on the high modulus of rupture and high modulus of elasticity sides as compared with the electrofused alumina aggregate based material A, and the structure of the AZ1 group became dense, high modulus of rupture and high stiffness as compared with the electrofused alumina. On the other hand, the group of ZM raw materials tend to have both low modulus of rupture and elasticity as compared with the A, indicating that it is effective for reducing the modulus of elasticity by adding them. AZ2 and AOC were located intermediate to AZ1 and ZM, but slightly lower modulus compared to the A. It was considered that both the modulus of rupture and modulus of elasticity of each material were determined depending on the denseness of the structure brought about by

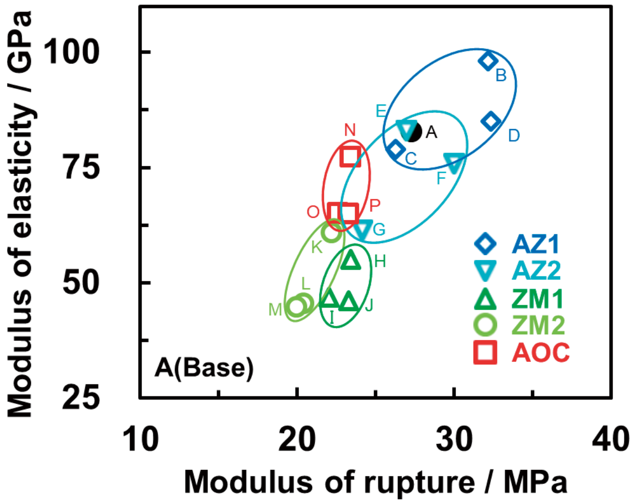

Fig. 5 Modulus of rupture plotted against modulus of elasticity for materials with each raw material system and base material (sample A).

3・2・2　耐熱衝撃性及び耐食性

耐熱衝撃性試験後サンプルの外観，横断面そしてその面内の貫通クラックの数を**図 6** に示す。貫通クラックの数とその大きさを比較すると，ベースと比較して AZ1 系原料添加サンプル（B, C, D）は貫通クラックの数，大きさ共に増加した。試験後サンプルの外観にも大きな亀裂が複数生じていた。AZ2（E, F, G）では添加量が増加しても貫通クラックの数は変わらないが，やや亀裂が小さくなった。ZM1 及び ZM2（H, I, J 及び K, L, M）では添加量増に伴って貫通クラック数が減少し，亀裂が小さくなった。一方，AOC（N, O, P）は 24 mass% までの添加で，貫通クラックの数が減少し，亀裂が小さくなったが，36 mass% 添加で貫通クラック数が再び増加した。以上の結果，AZ1 では，添加量の増加とともに耐熱衝撃性はやや低下し，AZ2 では添加量が多いほどやや改善される。ZM1 及び ZM2 においても添加量の増加とともに耐熱衝撃性が改善される。AOC では，24 mass% までの添加で改善するものの，36 mass% 添加では，耐熱衝撃性の低下を示した。赤峰ら[3]も，AOC 原料の多量添加において，高温加熱により AOC 原料自体の焼結が進行し，骨材周囲に空隙が形成され，耐熱衝撃性が低下する同様の結果を示している。全体的には，ZM2 を 36 mass% 添加したサンプル M が最も亀裂が軽微で，最良の耐

the mechanical properties such as the strength and the thermal properties such as thermal expansion inherent to each aggregate raw material.

3･2･2 Thermal shock resistivity and corrosion property

The appearance and the vertical cross section of the specimens after the thermal shock test, and the number of through cracks in the vertical cross section are shown in **Fig. 6**. When the number of through cracks and their size were compared, the number and size of through cracks were both increased in AZ1 based raw material added materials (B, C, D) compared with the base. Multiple large cracks were also seen in the appearance after the test. In the materials with AZ2 (E, F, G), the number of through cracks did not change even if the added amount increased, but the cracks slightly became small. In the materials with ZM1 and ZM2 (H, I, J and K, L, M), the number of through cracks decreased and the cracks became smaller with increasing the added amount. On the other hand, the materials with AOC (N, O, P) decreased the number of through cracks and the degree of cracking with the addition of up to 24 mass%, while the number of through cracks increased again with the addition of 36 mass%. From these results, in the materials with the AZ1, the thermal shock resistivity lowered slightly with increasing the addition amount, and in the materials with the AZ2, the thermal shock resistivity was improved slightly with increasing the addition amount. Thermal shock resistivity is improved in the materials with both ZM1 and ZM2 with increasing the amount. In the case of the AOC, although it was improved by the addition of up to 24 mass%, the addition of 36 mass% declined the thermal shock

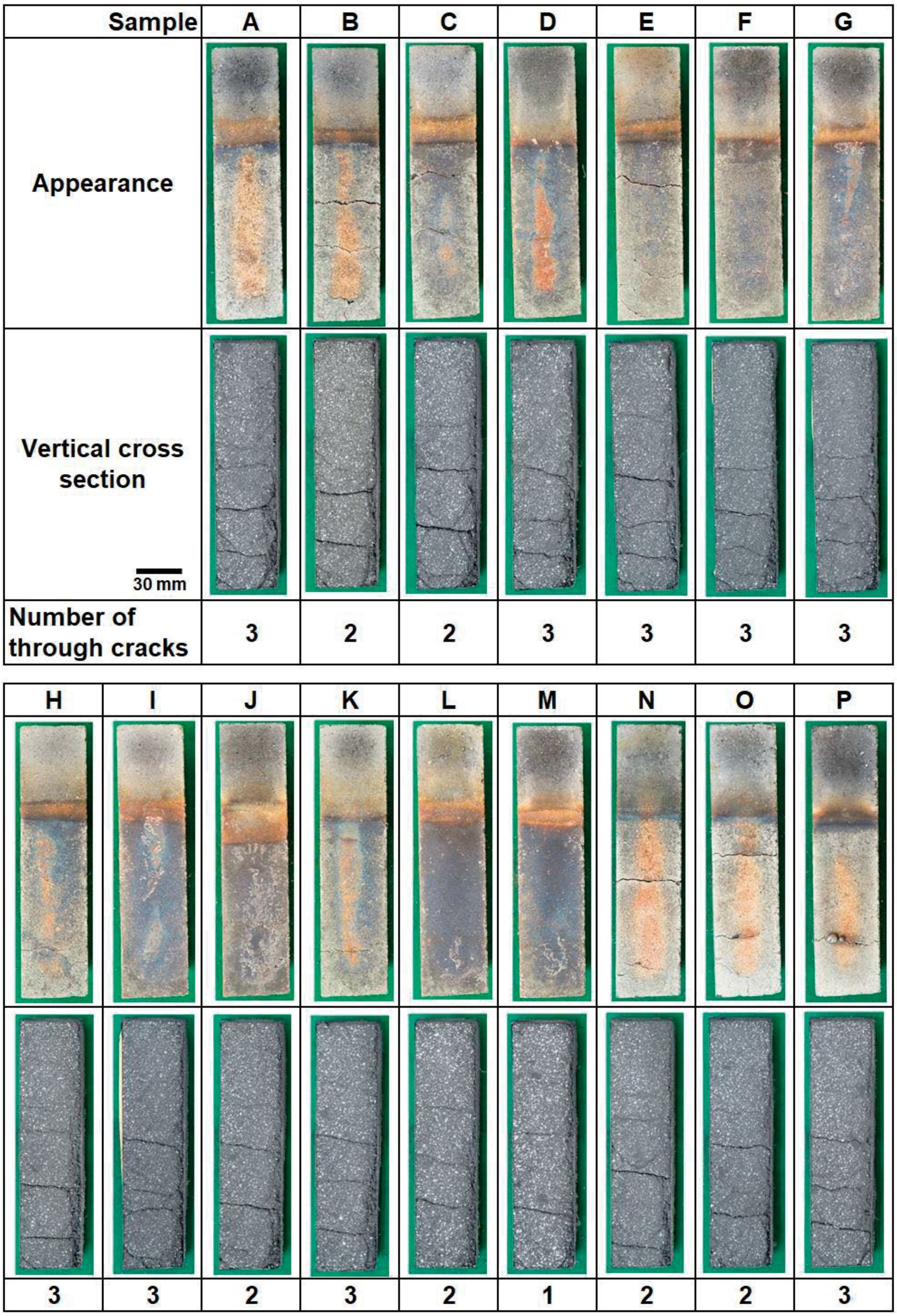

Fig. 6 Appearance and vertical cross section view of specimen and number of through cracks detected after thermal spalling test in each sample.

熱衝撃性を示した。

耐食性評価試験後のサンプル断面を**図 7** に，溶損指数算出による評価結果を**表 4** に示す。まず溶損速度は，**図 7** の各サンプルの最大減寸量，つま

resistivity. Akamine et al.[3] also show a similar result in which, in a large amount of the AOC aggregate raw material added, the thermal shock resistivity is lowered by voids forming around the aggregate with sintering itself during the high temperature firing. The best thermal shock resistivity with the least

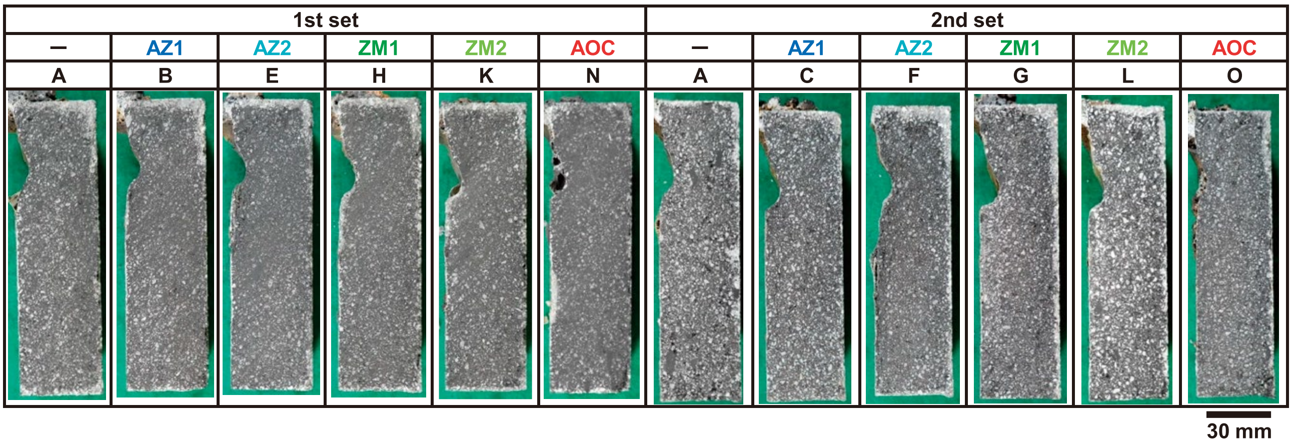

Fig. 7 Appearance of cross section of the selected specimens after corrosion tests of 1st and 2nd set.

Table 4 Results of corrosion test expressed by corrosion index* for all the samples tested

Sample	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P
Raw material system	-	AZ1			AZ2			ZM1			ZM2			AOC		
Amount / mass%	0	12	24	36	12	24	36	12	24	36	12	24	36	12	24	36
1st set	100	103			115			118			125			73		
2nd set	100		104			125			120			115			87	
3rd set	100			126			122			147			164			100

*Corrosion index: 100 as base material (sample A) and values >100 is superior and <100 is inferior the corrosion property than the base material.

り各サンプル断面に見られるくぼみの深さを測定し，それを浸漬時間で割ることによって求めた。次に，各試験セットのベースサンプルAの溶損速度を100とし，他のサンプルの溶損速度を100に対する比で表したものを溶損指数としている。いずれの骨材種でも添加量が多いほど，溶損指数は大きくなり耐食性の低下を示した。AZ1ではベースとほぼ同等程度の耐食性を示したが，AZ2ではベースよりも溶損指数はやや大きく，スラグライン下のメタル浸漬部に組織の脆化が見られた。これはAZ2が高い残存膨張を示すため，高温下で脆弱化が進行したことによるものと考えられた。ZMでは溶損指数はさらに大きく，添加量が多いほど耐食性の著しい低下が見られた。これはZM系原料に含まれるSiO_2がスラグと反応することにより，溶損が進行したためと考えられた。一方，AOCではベースサンプルAよりも優れた耐食性を示した。高杉ら[10]も，AOC原料がアルミナ原料より優れた耐食性を有するという同様の結果を示している。

cracking in total was exhibited by the material M with ZM2 added in 36 mass%.

Figure 7 shows the cross section view of the specimens after the corrosion test, and **Table 4** shows the results determined in terms of the corrosion index. First, the corrosion rate was determined by measuring the maximum size reduction of each specimen in **Fig. 7**, i.e., the depth of the valley bottom of the indentation found in each specimen cross section, and dividing it by the immersion time. Next, setting the corrosion rate of the base sample A of each test set to 100, and the corrosion rate of the other samples expressed by the ratio to 100 is set as the corrosion index. The higher the addition amount of any aggregate species, the higher the corrosion index with lowering the corrosion resistance. In **Table 4**, the group of AZ1 showed almost the same degree of corrosion resistance as the base, but the AZ2 showed a little higher corrosion index than the base, and embrittlement of the structure was found in the molten metal immersed part below the slag line. Since the AZ2 had higher residual expansion, the increased fragility at high temperature, caused the structural weakening. In ZM, The corrosion index was further high, showing a noticeable loss in the corrosion resistance with increasing the added amount of the aggregate. Such as intensified corrosion

4　結論

高温焼成したSNプレート材質の諸特性に及ぼすZrO_2含有及びAl_4O_4C骨材原料の添加効果を調査した結果，以下の知見が得られた。

1）ZrO_2含有骨材原料は，原料自体の緻密さと，晶出するバデライト（単斜晶系のZrO_2）の相転移に起因した特異な膨張挙動が，それを添加した材料内部の組織の緻密さ，さらには強度や弾性率等の特性に影響を与えた。緻密で膨張のヒステリシスが小さいAZ1を添加すると，見掛気孔率が低くなり，高強度，高弾性率となった。また，膨張のヒステリシスが大きいSiO_2含有原料のZM1及びZM2を添加すると，見掛気孔率が高くなり，強度，弾性率は低下した。

2）AOC原料は，ZrO_2含有原料と比較して直線的な膨張挙動を示すが，特異な焼結特性を持つことから、焼成時の条件によって，それを添加した材料の組織や強度，弾性率へ影響を与える可能性が示唆された。

3）耐熱衝撃性は，弾性率を低減する効果が高いZM1，ZM2の添加量が増えるほど向上した。AZ1は強度や弾性率を向上する効果があるため，添加量が多いほど耐熱衝撃性が低下した。AZ2は添加量が多いほど耐熱衝撃性がやや向上する傾向が見られたが，長時間もしくは繰り返し熱履歴を受けると組織の脆化が懸念された。AOCは24 mass% 添加では改善するが，36 mass% 添加で耐熱衝撃性の低下が見られた。

4）耐食性は，AOC原料を24 mass% 以下添加したサンプルにおいてのみベース材より改善が見られた。ZrO_2含有原料はいずれも，添加量が多いほど耐食性は低下し，特にSiO_2を含有するZM系原料は大きく低下した。

5）耐食性及び耐熱衝撃性の両方を向上させたい場合，AOC原料を12～24 mass% の範囲で添加することが効果的であった。

occurred by vigorous reaction of SiO_2 contained in ZM aggregates with the slag as the corrosive agent. The materials with the AOC raw material, however, had only superior corrosion resistance to the base material A (the material with the alumina raw material) similarly to the report by Takasugi et al.[10]

4 Conclusions

The effects of adding ZrO_2 containing raw materials and Al_4O_4C raw materials on the characteristics of high temperature fired SN plate materials were investigated and the following results were obtained.

1) In the ZrO_2 aggregate raw materials, the denseness of the raw materials themselves and the peculiar expansion behavior due to the phase transition of the baddeleyite (monoclinic ZrO_2) affected the denseness of the structure inside the materials to which they were added, and the properties such as strength and modulus of elasticity. When the AZ1 which is dense and has less hysteresis of expansion is added, a low apparent porosity is obtained, resulting in a high strength and high modulus of elasticity. Further, when the ZM1 and the ZM2 raw materials containing SiO_2 having a large hysteresis of thermal expansion are added, a high apparent porosity with lowered strength and the modulus of elasticity is obtained.
2) The AOC raw material showed a linear expansion behavior different from the ZrO_2 containing raw materials, but it had a peculiar sintering behavior to form voids around the AOC grains during firing process, such behavior might affect the structure, strength, and modulus of elasticity of the material depending on the firing procedure.
3) Thermal shock resistivity was improved with increasing amounts of the ZM1 and ZM2 added, respectively, by lowering the modulus of elasticity much effectively. The materials with the AZ1 added lowered the thermal shock resistivity by increasing the strength and the modulus of elasticity with increasing amount of the AZ1. The materials added AZ2 showed a tendency to slightly improve the thermal shock resistivity as the added amount increased, but these are some concerns about the embrittlement of the structure of the material when subjected to a long term or repeated heating practices. The AOC improved the resistivity by the additions up to 24 mass%, but for the the addition of 36 mass% resistivity lowered slightly due to the peculiar sintering behavior described in 2).
4) Corrosion resistance was improved from the base material only in the materials with the AOC raw material added 24 mass% or less. For all the ZrO_2

containing raw materials, the corrosion resistance lowered with increasing the added amount of them, in particular the ZM raw material containing SiO_2 lowered the corrosion resistance largely.

5) When it is intended to improve corrosion resistance and thermal shock resistance of the SN plate material, it was effective to add AOC raw material in amount of 12～24 mass%.

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本報告は，以下の報文に，加筆，再構成して転載したものである。
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