

SHINAGAWA TECHNICAL REPORT

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Characteristics of Castable Refractories for Steel Ladle Heated under Restraint

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品川技報

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要 旨

取鍋用流し込み材として主に使用されるアルミナ-マグネシア材質は高温でのスピネル生成反応にともなって大きな残存膨張を示し、組織が多孔質となることが知られている。しかし、実際の取鍋における使用時には構造上、周囲を二軸で拘束された状態で加熱、使用される。そのため、試験室での評価時と実機使用時では組織、特性に差が生じる。そこで、本研究では実炉に近い拘束条件下での加熱試験を試み、二軸拘束状態での加熱の影響を調査した。検討の結果、試験片の周囲にキャストブルを施工することによって拘束状態での加熱を行うことができた。また、拘束下での加熱による緻密化の進行が確認できた。特に高温において大幅な強度の増大が認められ、実機使用時には非拘束加熱による評価から見積もられるよりも稼働面と背面側との間に大きな強度ギャップが生じていることが示唆された。

Abstract

Alumina-magnesia castable materials used mainly in steel ladles form spinel at high temperatures heated under free conditions results in large permanent linear change and the material texture becomes porous. The materials are used as a structure in actual use and are bi-axially restrained by the surrounding structural members. It is known that the textures and characteristics of the materials in actual use do not match the laboratory evaluations. This study investigated the influence of bi-axial restraint on the characteristics of alumina-magnesia castable refractories. The other castable material with high strength was cast to the surrounding area of the alumina-magnesia castable to prepare bi-axially restrained specimens. Densification of the specimen texture was observed after heating under restraint. The strength was greatly increased especially after heating at high temperature. This suggests that the difference in the strength between the working face and backside of actual ladles is significantly larger than the material evaluations carried out under non-restrained conditions.

1. 緒言

現在、溶鋼取鍋内張り用不定形材料にはアルミナ-マグネシア質流し込み材が広く用いられている。アルミナ-マグネシア材質は、アルミナ原料

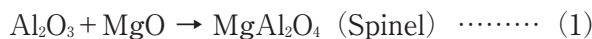
1. Introduction

Alumina-magnesia castable refractories have been widely used for working linings of steel ladles. They are composed of alumina and

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とマグネシア原料を組み合わせた材質であり¹⁾⁻³⁾、加熱時に両者が反応して以下の(1)式に従いスピネルを生成する。



生成した均一なスピネル相により、高耐食性、高耐スラグ浸潤性の特性を有している。

また、アルミナ-マグネシア材質は熱膨張において特徴的な挙動を有し、スピネルの生成反応にともなって1200℃～1400℃において急激な膨張を示し、冷却後も残存する (Fig.1)。また、この膨張は気孔率の増大を伴い、多孔質な組織となる。しかし、一方で実機における使用に際しては周囲の材質や鉄皮によって拘束された状態にあるため、膨張は構造的に制限されることになり、また材料が荷重軟化挙動を示すため⁴⁾、試験室での評価時のような解放状態で加熱した場合と比較して緻密化するものと考えられる。

最近の報告において、拘束下での加熱試験の結果が報告されており、北中ら⁵⁾は両端を固定した状態での加熱試験を行い、拘束下での加熱によって亀裂の発生、座屈に至る結果を報告している。また、神尾ら⁶⁾は両端を拘束した試料を用いた急加熱試験を行い、亀裂成長に関する観察結果を報告している。しかし、取鍋実機においては周囲を拘束され稼働面側に解放状態にある、すなわち二軸拘束の状態にあるので一軸の拘束は必ずしも取鍋実

magnesia raw materials¹⁾⁻³⁾、 and spinel is formed by the following reaction (1).



The formed spinel gives the good effects of the high corrosion resistance and high slag penetration resistance.

Alumina-magnesia materials expand drastically at 1200℃-1400℃ and the expansion remains after cooling under non-restrained conditions (Fig.1). The expansion causes an increase in apparent porosity and the material texture becomes porous. However, in actual use, the expansion is limited by the surrounding structural members and steel shell. In addition, the refractories show creep behavior at high temperature⁴⁾. The material texture under restraint is considered to be denser than that under non-restrained conditions as in laboratory evaluations.

In the recent researches, the heating tests under restrained conditions have been reported. Kitanaka et al.⁵⁾ carried out heating tests with the specimens fixed at the both ends and reported that the specimens were cracked and buckled. Kamio et al.⁶⁾ conducted rapid heating tests with the specimens fixed at both ends and reported about the observations of crack-developing behavior. However the refractories used in actual steel ladles are under bi-axial restraint and are free in the direction perpendicular to the hot face. The examinations under uniaxial restraint such as the above do not fit the actual use conditions in steel ladles. In this study, we heated specimens under bi-axial constraint and investigated the change in the material characteristics.

2. Heating Test under Restraint

2. 1 Preparation of restrained specimens

The outline of the restrained specimen is shown

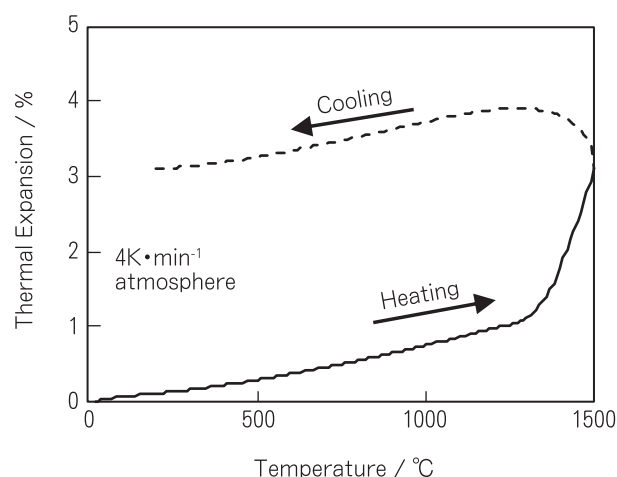


Fig.1 An example of thermal expansion behavior of alumina-magnesia castable refractories.

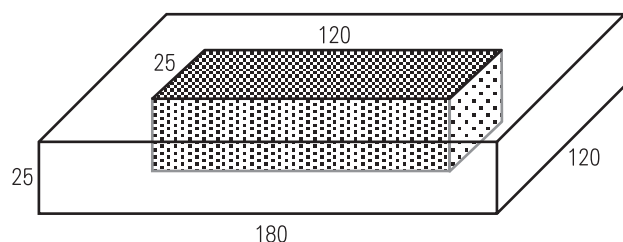


Fig.2 Schematic diagram of restrained specimen.

機の状態を再現するものではない。そこで本研究ではより実機に近い二軸拘束状態での加熱試験の実施を試み、拘束加熱による材料特性の変化について調査を行った。

2. 拘束下加熱の実施

2. 1 拘束試料の作成

Fig.2に拘束加熱用試料の概略図を示す。試験片は試料キャストブルを25mm×25mm×120mmの型枠に鑄込み、24時間以上養生して作成した。この試験片を120mm×25mm×180mmの型枠中央に置き、周囲に外周キャストブルを流し込んで24時間以上養生後脱枠し、110℃で24時間乾燥して拘束試料とした。また、比較対象として、試験片を110℃で24時間乾燥して非拘束試料を作成した。

試料キャストブルおよび外周キャストブルの仕様をTable 1に示す。試料キャストブルはMgO添加量が3%から11%のアルミナ-マグネシア質流し込み材を用いた。外周キャストブルは耐スポーリング性に優れ、残存線変化の小さいアルミナ-シリカ質の材質を選定した。

これら拘束、および非拘束の試料を1000℃、1300℃、1500℃の各温度、大気雰囲気中で3時間の加熱を行った。

2. 2 拘束下加熱結果

Fig.3にMgO 11%の拘束試料の1500℃加熱後の外観を示す。試験片、外周キャストブルとも亀裂の発生は認められなかった。拘束試料と非拘束試料の加熱後残存線変化率をFig.4に示す。残存線変化率の測定は外周キャストブルを除去したうえで、試験片の長辺方向で測定した。非拘束試料は加熱温度が上昇するにしたがって残存膨張が大きくなったのに対し、拘束試料ではいずれの温度に

Table 1 Specifications of sample castables and outer castable

		Sample Castable			Outer Castable
		(a)	(b)	(c)	
Chemical composition / %	Al ₂ O ₃	87	91	95	57
	MgO	11	7	3	—
	SiO ₂	1	1	1	39
Maximum particle size / mm		5	5	5	5
Water content / %		5.5	5.5	5.5	6.5

in Fig.2. The castable specimens were prepared by casting into a 25mm×25mm×120mm mold and were cured over 24 hours. They were put at the center of another 120mm×25mm×180mm mold and the other castable material (hereafter “outer castable”) was cast to the surrounding area of the specimens to be restrained. They were cured over 24 hours and were dried at 110℃ for 24 hours. For comparison, the non-restrained specimens without outer castable were also prepared by the same curing and drying methods.

The specifications of the specimens and the outer castable are shown in table 1. The specimens were alumina-magnesia castable refractories containing 3% to 11% of MgO. The outer castable had good spalling resistance and small permanent linear change.

The restrained and non-restrained specimens were heated at 1000℃, 1300℃ and 1500℃ for 3 hours in air.

2. 2 Results of heating test under restraint

Figure 3 shows the appearance of the restrained specimen containing 11% MgO after heating at 1500℃. No cracks were found on the specimen or outer castable. Figure 4 shows the permanent linear changes of the restrained and the non-restrained specimens. The permanent linear change was measured in a longitudinal direction after removing the outer castable in case of the restrained specimen. The expansion

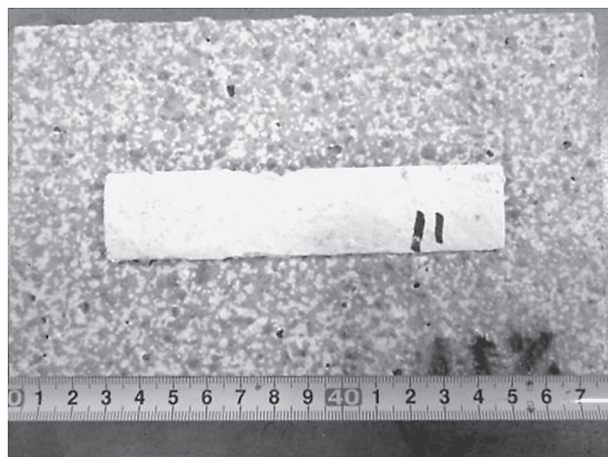


Fig.3 Restrained specimen after heating at 1500°C.

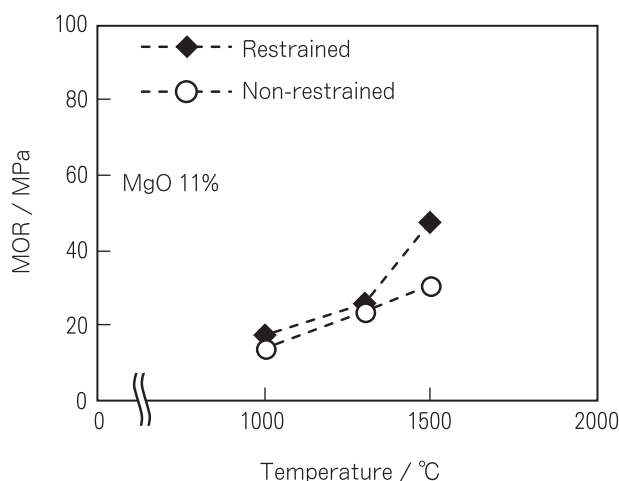


Fig.5 Modulus of rupture of restrained and non-restrained specimens at various temperatures.

においても残存膨張はみられなかった。

アルミナ-マグネシア材質は大きな残存膨張を示す材質であるが、周囲を二軸で拘束した場合には一軸で拘束した場合にみられるような亀裂や座屈⁵⁾によって応力が緩和されず、膨張を抑制した状態で加熱されることが確認できた。

これら拘束、および非拘束試料について各種特性の評価を行った。

3. 拘束による材料特性の変化

3.1 加熱後材料特性の比較

MgO 11% (Table 1の配合 (a)) の拘束試料および非拘束試料について、各加熱温度における材料特性の比較を行った。

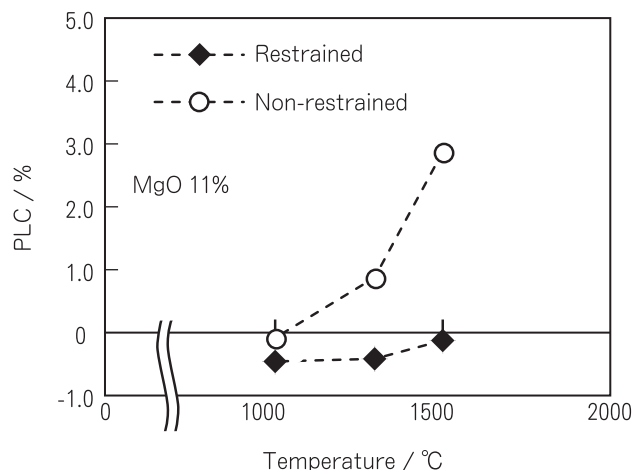


Fig.4 Permanent linear change of restrained and non-restrained specimens at various temperatures.

of the non-restrained specimens increased according to higher heating temperature, on the other hand, expansion of the restrained specimens was almost zero at all heating temperatures.

The alumina-magnesia refractories show large permanent linear change. However, the specimens heated under bi-axial restraint suppressed the expansion regardless of no stress relaxation by fracture behaviors such as cracks and buckling⁵⁾.

We evaluated various characteristics of the specimens heated under restraint and non-restraint.

3. Change in Characteristics under Restraint

3.1 Characteristics comparison after heating

The samples containing 11% of MgO (sample (a) in Table 1) were heated at high temperature under restrained and non-restrained conditions. The characteristics were measured and evaluated.

Figure 5 shows the modulus of rupture (hereafter MOR) after heating. The MOR of

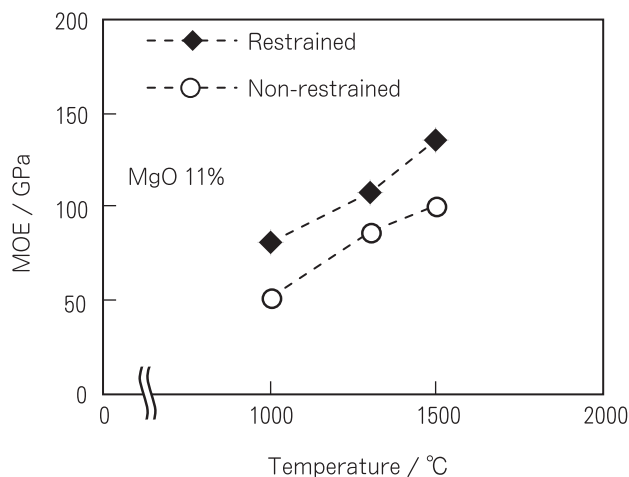


Fig.6 Modulus of elasticity of restrained and non-restrained specimens at various temperatures.

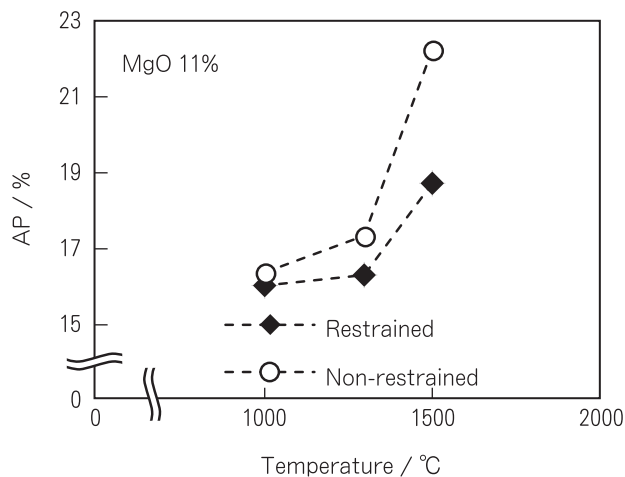


Fig.7 Apparent porosity of restrained and non-restrained specimens at various temperatures.

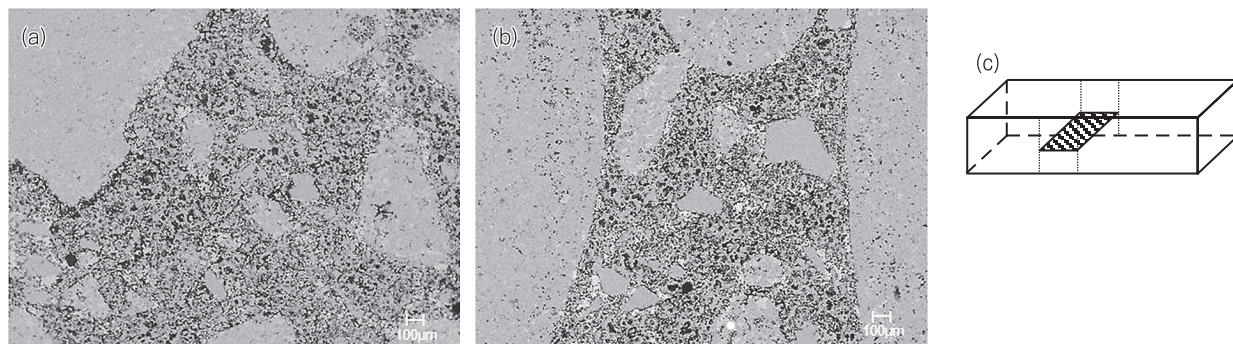


Fig.8 Microscope image of (a) non-restrained specimen; (b) restrained specimen; (c) schematic diagram of sampling position.

Fig.5に加熱後の曲げ強さを示す。非拘束の試料においても加熱温度が高いほど曲げ強さが増したが、拘束下で加熱した試料はより強度の増大が顕著であり、特に1500℃で加熱した場合に大幅に強度が高くなる結果が得られた。Fig.6に加熱後の弾性率測定結果を示す。いずれの加熱温度においても拘束条件で加熱した試料の方が高い値を示した。Fig.7に見掛け気孔率を示す。拘束、非拘束いずれの試料においても加熱温度が高くなると気孔率は増大する傾向を示したが、拘束試料は気孔率の増大が抑制され、非拘束の場合と比較して低気孔率で緻密になる結果が得られた。

3. 2 拘束/非拘束試料の微構造観察

Fig.8はMgO 7%の試料における1500℃加熱後

both of them increased with the higher heating temperature. The MOR of the restrained specimens increased more especially when heated at 1500℃. Figure 6 shows the modulus of elasticity (hereafter MOE) after heating. The MOEs of the restrained specimens were higher than those of the non-restrained specimens throughout the heating temperature range. The change in apparent porosity (hereafter AP) is shown in Fig.7. The AP of both increased with temperature. The AP of the restrained specimens increased less than the non-restrained specimens, which means that the restrained specimens had a denser texture than the non-restrained ones.

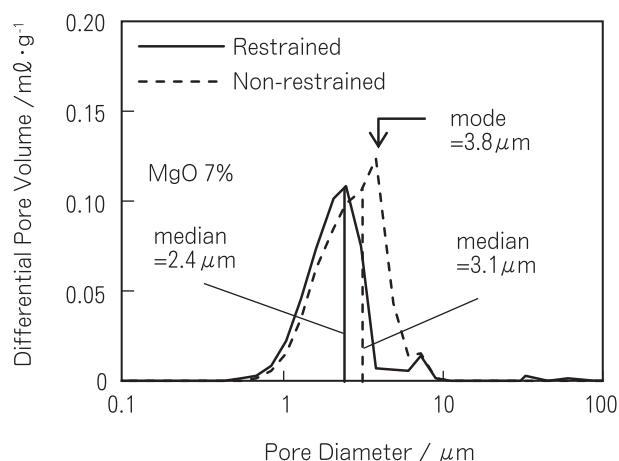


Fig.9 Pore-size distribution of restrained and non-restrained specimens after heating at 1500°C.

の反射電子像による組織写真である。Fig.8(a)に非拘束試料、(b)に拘束試料の組織写真を示す。観察試料は拘束面内で採取した (Fig.12 (c))。非拘束試料の方が黒く写った気孔が多く組織が多孔質になっており、拘束試料は気孔が少なく、緻密な組織となっている様子が認められた。

気孔径への影響を調べるため、水銀圧入法により気孔径分布を測定した。Fig.9にMgO 7%の試料における測定結果を示す。拘束試料は気孔のメディアン径が $2.4\mu\text{m}$ で、非拘束試料では気孔のメディアン径が $3.2\mu\text{m}$ であったのに対して気孔が微細なものとなっていた。また、非拘束試料でみられる $3.8\mu\text{m}$ 付近の最大ピークが拘束試料では大幅に小さくなっていた。

3. 3 拘束による材料特性の変化

試験片を外周キャストブルに埋め込んで加熱することによって残存膨張が抑制されており、二軸拘束下で座屈しない試料を作成できた。拘束下で加熱することによって気孔率の低下と気孔の微細化、強度および弾性率の増大、気孔率の低下が認められた。拘束下での加熱によって材料が緻密になり、強度、弾性率に増大につながったものと考えられる。

3. 2 Microstructures of restrained and non-restrained specimens

Figure 8 shows the compositional images of the specimens containing 7% of MgO heated at 1500°C Fig.8(a) is an image of the non-restrained specimen and Fig.8(b) is an image of the restrained specimen. The images were taken parallel to the restraint plane (Fig.8(c)). In the photos, the black area and dots indicate pores. The non-restrained specimens had more pores and a more porous texture. The restrained specimen had less pores and denser texture.

To investigate the influence of restraint on pore size, the pore size distribution of the specimens containing 7% MgO was measured by mercury porosimeter (Fig.9). The median pore size of restrained specimen was $2.4\mu\text{m}$, which is smaller than that of the non-restrained specimen at $3.1\mu\text{m}$. Moreover, the largest peak of non-restrained specimen at $3.8\mu\text{m}$ was drastically reduced in the restrained specimen.

3. 3 Change in characteristics under restraint

Outer castable suppressed the permanent linear change of the specimens. The specimens showed no cracks or buckling after heating under bi-axial restraint. Porosity reduction, pore refinement, MOR and MOE increase were observed. It is considered that texture densification caused by heated under restraint results in increase of MOR and MOE.

4. Influence of MgO Content on Physical Characteristics after Heated under Restraint

4. 1 Influence of MgO content on permanent linear change

We evaluated the influence of MgO content on material characteristics after heating under restraint (Table 1 (a)-(c)). The change in permanent linear change (hereafter PLC) according

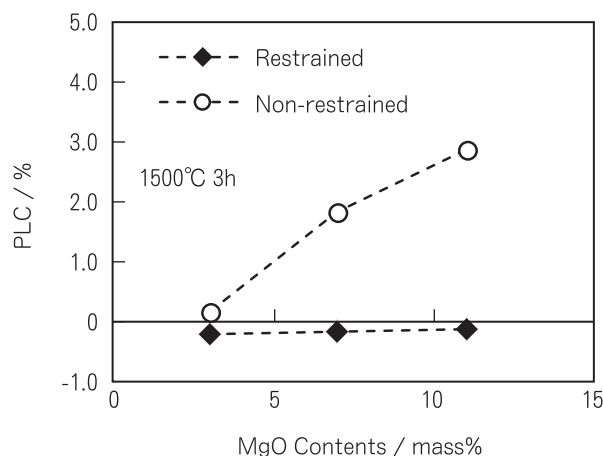


Fig.10 Permanent linear changes of restrained and non-restrained specimens with various MgO contents.

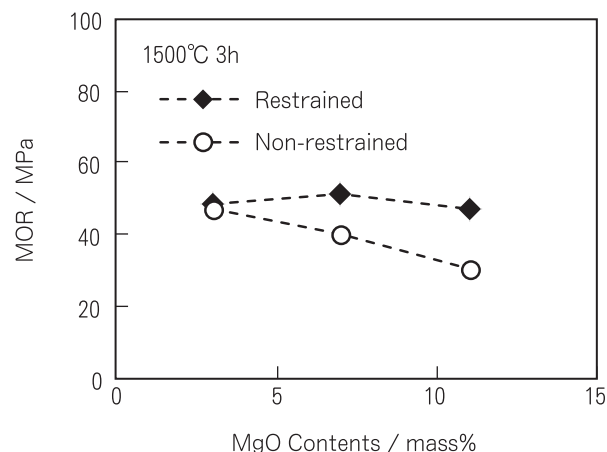


Fig.11 Modulus of rupture of restrained and non-restrained specimens with various MgO contents.

4. 拘束下加熱におけるMgO添加量の影響

4. 1 MgO添加量の異なる試料での拘束下加熱

MgO添加量の異なる配合 (Table 1(a)-(c)) で、拘束加熱試験を行い、MgO添加量の影響を評価した。Fig.10に残存線変化率を示す。非拘束試料ではMgO添加量が多くなると残存膨張率は大きくなる傾向を示す。一方で、拘束試料においてはいずれのMgO添加量においても残存膨張はみられず、拘束された状態での加熱を行うことができていたものと考えられる。また、MgO添加量3%の試料は非拘束の試料でも残存膨張を示さず、拘束、非拘束で差はみられなかった。

4. 2 MgO添加量の材料特性への影響

MgO添加量の異なる試料について、拘束下加熱後の特性を評価した。Fig.11に曲げ強さを示す。非拘束試料ではMgO添加量が多くなるほど強度が低下する傾向を示した。一方で拘束試料はMgO添加量による変化はほとんど見られず、いずれの添加量においても非拘束試料と同等以上の強度を示した。Fig.12に弾性率を示す。弾性率は拘束試料、非拘束試料ともMgO添加量が多いほど低下する傾向を示し、低下の程度は非拘束試料の方が顕著であった。Fig.13に見掛け孔率を示す。拘束、非拘束ともMgO添加量が多くなると増大する傾向を示し、増大は非拘束試料で顕著であった。

to the MgO content is shown in Fig.10. The PLC after heating under non-restrained conditions increased as the MgO content increased. On the other hand, PLC after heating under restrained conditions, the PLC remains about the same throughout the whole heating temperature range. It is considered that the restrained specimens were heated in enough restrained conditions. The specimens containing 3% MgO heated under both of restraint and non-restraint showed almost zero PLC.

4. 2 Influence of MgO content on physical characteristics

We evaluated the change in the physical characteristics against MgO content after heating under restrained conditions. Figure 11 shows the change in MOR. After heating under non-restrained conditions the MOR lowered as the amount of MgO increased. On the other hand, the MOR was not influenced by the content of MgO and remained almost same after heating under restrained conditions. The restrained specimens show the same or higher MOR than the non-restrained one for each MgO contents. Figure 12 shows the change in MOE in relation to the MgO content. The MOE of both the

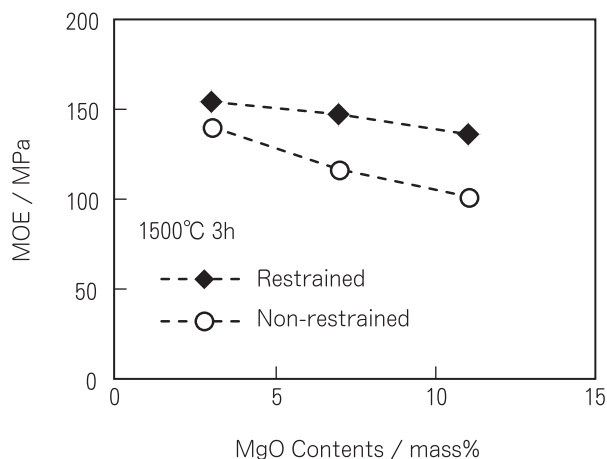


Fig.12 Modulus of elasticity of restrained and non-restrained specimens with various MgO contents.

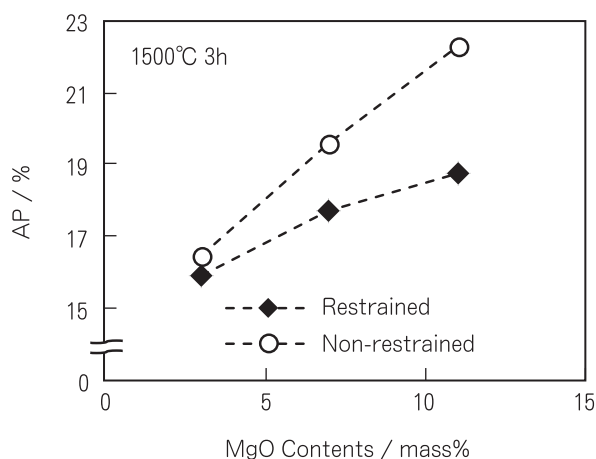


Fig.13 Apparent porosities of restrained and non-restrained specimens with various MgO contents.

4. 3 拘束下加熱におけるMgO添加量の影響

MgO添加量が少ない3%の試料では、非拘束の条件でも残存膨張をほとんど示さず、拘束・非拘束条件間で材料特性の変化はほとんど見られなかった。一方、MgOの多い11%の場合には非拘束の条件での残存膨張が大きくなり、拘束と非拘束との強度の差が大きくなった。

一方で拘束下ではMgO添加量に関わらず残存膨張は認められないのに対し、MgO量の増加に対して見掛け気孔率は増大、弾性率は低下する傾向を示した。本試験では試料の拘束条件を二軸として

restrained and the non-restrained specimens decreased as the MgO content increased. The MOE of the non-restrained specimens decreased more markedly than those of the restrained specimens for each MgO contents. Figure 13 shows the change in AP. The AP of both the restrained and non-restrained specimens rose up as the content of MgO increased. The AP values of the non-restrained specimens rose up more significantly than those of the restrained.

4. 3 Influence of MgO content on physical characteristics after heating under restraint

The PLCs of the specimens containing 3% of MgO were almost zero after heating under not only restrained but also non-restrained conditions. The physical characteristics did not show significant difference between the restrained and the non-restrained specimens. On the other hand, the PLCs of the specimens containing 11% MgO after heating under restraint were larger than those under non-restraint resulting in lower MOR.

The PLCs of the restrained specimens were approximately zero regardless of the increase in AP and decrease in MOE as the MgO content increased. The bi-axially restrained specimens are considered to have expanded in the direction perpendicular to the restrained axis, and the material texture became porous.

5. Influence of Restraint in Actual Use

The MOR of the restrained specimens heated at high temperature significantly increased in comparison with those of the non-restrained specimens. This suggests that the difference in the material strength between the hot face and backside of the ladles will be more significant than the estimated under non-restrained conditions in laboratory, especially in case of the materials which have large MgO content and

いるので、拘束されていない上下方向で膨張が起こり、材料の多孔質化が進行したことが考えられる。

5. 実炉使用時の影響

拘束条件下で加熱を行うと、高温で加熱された場合に非拘束の場合と比較して強度が急激に上昇する結果が得られた。そのため、特にMgOが多く残存膨張が大きい場合には試験室での非拘束加熱による評価から見積もられるよりも稼働面と背面側との間に大きな強度ギャップが生じていることが示唆された。

またMgO添加量が多くなると、拘束面内での線膨張が認められないにも関わらず気孔率の増大が認められ、非拘束軸方向へ膨張していることが考えられる。そのため、一軸拘束条件での加熱試験でみられるような亀裂^{5), 6)}が実機使用においてスポーリング損傷として顕在化することが考えられる。添加MgOを増量することで耐食性を向上できる¹⁾が、稼働面強度増大による強度ギャップの発生、非拘束軸方向への膨張の発生には留意が必要と考えられる。

6. まとめ

アルミナ-マグネシア質流し込み材について、より実機に近い条件での評価を目的に、二軸拘束下での加熱試験を行った。試験片を拘束して加熱することで、残存膨張は抑制され、組織が緻密化することが実験的に確認できた。

今後、実機使用の条件と比較、試験方法の改良を行い、より実機の状況に見合った評価方法の確立を検討していく。

larger PLC.

The alumina-magnesia materials containing much MgO showed a very small PLC in the restrained directions, however, the AP increased. The materials are considered to have expanded in the direction perpendicular to restrained axis. Spalling can occur in actual use with materials that spalled in the uniaxial restraint tests^{5), 6)}. Corrosion resistance can be improved by increasing the content of MgO¹⁾, but it is necessary to pay attentions to the significant difference in material strength between the hot face and backside of the ladles, and material expansion in the direction perpendicular to the restrained axis.

6. Conclusion

In order to evaluate the characteristics of alumina-magnesia castable refractories in conditions similar to those of actual use, heating tests under bi-axial restraint were conducted. It was experimentally confirmed that the PLC of the restrained specimens after heating was very small and the texture became denser.

Hereafter, we would like to compare the results of experiments and actual use and improve the examination methods. Moreover, we will make efforts to establish better evaluation methods reproducing actual conditions.

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