

SHINAGAWA TECHNICAL REPORT

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熱間補修用特殊珪石れんがの特徴

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in the Coke Oven Wall for 8 Years

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品川技報

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要 旨

日本で8年使用された当社の熱間補修用特殊珪石れんがHRSの解析を行った。

炭化室側は未使用HRSの組織に近いが、非晶質シリカが減り、クリストバライトが増えた微構造であった。一方、燃焼室側は、炭化室側と同レベルのクリストバライト量だが、非晶質シリカがさらに減ってトリジマイトが増え、また、組織は粗粒の分解と微粉化及びそれら微粉の結合が始まりつつある状態であった。炭化室面に若干の面損傷があり、全体に、化学成分の外部からの侵入は少なく、高強度化、若干の熱膨張率増加の傾向があったが、引き続き使用可能と推定された。

Abstract

Hot repairing silica bricks –HRS brand produced by Shinagawa Refractories Co., Ltd.– which were used for 8 years in Japan were analyzed. In the coke chamber side of the used HRS bricks, they showed a decrease in non-crystalline silica and an increase in cristobalite, although the texture resembled that of unused HRS bricks. In the flue chamber side of the used HRS bricks, the amount of non-crystalline silica was reduced further than that in the coke chamber side and the amount of tridymite increased more than that in the coke chamber side, although the amount of cristobalite was almost the same as that in the coke chamber side. Further, the texture was in a state where coarse grains were micronized and changed to the binding of fine grains. Little occurrence of surface damage on the coke chamber side, the little penetration of external chemical compositions into the bricks, increase in strength and a tendency for the thermal expansion ratio to increase were shown in the present studies. Even then, the 8 years used bricks were supposed to be successively enabled.

1. はじめに

珪石れんがはコークス炉の長期稼働を可能としたが、別項の44年使用珪石れんがのように長期間使用されると、途中の補修技術が重要になる。炭化室壁損傷の初期、中期段階では熱間吹付けないし溶射補修技術で対応できるが、後期になると、熱間

1. Introduction

When silica bricks have been used for a long time such as the 44 year used bricks shown in an other report, the technique for repairing becomes more important during the service. In the early and middle service life damage of the coke oven wall, hot or flame gunning are

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積替え補修技術が必要になる¹⁾。熱間積替え補修は、窯口での小規模補修から窯全長に渡った大規模補修までできる技術である²⁾。

熱間積替え補修用として当社で開発された特殊珪石れんがHRSは一般の珪石れんがと同等のSiO₂値を持ちながら室温から500℃までの急熱スパーリングに耐用する特徴を有し、熱間容積安定性に優れている^{1),3)}。また、この補修用れんがHRSは一般の珪石れんがに近い組織であり、15ヶ月使用HRSは8ヶ月使用の一般珪石れんがとトリジマイト結晶成長に違いがないこと、15ヶ月使用されても組織劣化はないことがわかっている³⁾。しかし、その後の経時変化の様子はあまり追跡されていない。今回、およそ3年、6.4年、8年使用の熱間補修用特殊珪石れんがHRSを調べることができた。本報では、その経年変化の様子を中心にして報告する。

2. 試料採取位置とれんが面観察

試料は、コークスサイド付近から採取された当社の熱間補修用特殊珪石れんがHRSである。

Fig.1に切断面写真を示す。れんが上面側の一部に欠けが見られるが、これらは使用時の損傷ではなく、炭化室壁の解体冷却時に生じたものである。いずれの試料も燃焼室側に損傷はなく、炭化室側はほぼ原寸ではあるが若干の面損傷が認められる。経年の違いはほとんどない。ダボ形状を含む欠け部以外の残存部分は健全な状態であった。

切断面を見ると、3年、6.4年、8年使用れんがでは、白色の粗粒がれんが内にほぼ一様に認められるが、未使用HRSれんがでは透明感のある粗粒である。シリカの転移による違いであり、少なくとも3年使用で透明感のある粗粒は見られなくなっている。また、切断面の色調の違いを見ると、3年使用はほとんど同一の色調、6.4年はほぼ同一だが若干の違いがあり、8年使用では炭化室側、中間部、燃焼室側で色調が異なって見え、3つに区分できる。以下では、いずれの試料も炭化室側から燃焼室側に向かって3つの層に分けて調べた。

effective for repairing the damage. However, in the later service life, hot exchange repair is required¹⁾, because it has advantages for both small-scale repairing in the oven front and large-scale repairing over the entire oven length²⁾.

HRS brand silica bricks, which were developed for hot repairing by Shinagawa Refractories Co., Ltd., have almost the same SiO₂ content as conventional silica bricks. In addition, they have excellent thermal spalling resistance during the rapid heating of R.T. up to 500℃ and first-class volume stability at elevated temperatures^{1),3)}. Further, the texture of the HRS bricks was found to be similar to that of conventional silica brick. The tridymite growth of the 15 month used HRS bricks was almost the same as that of the 8 month used conventional brick and deterioration of the HRS brick microstructure did not occur during a 15 month operating period³⁾. However, the influence of secular change after 15 months has not been studied thoroughly and systematically. This time, we had a good chance to investigate HRS brand hot repairing silica bricks which have been used for about 3, 6.4 and 8 years. The core of this report is about the secular changes of used bricks' features.

2. Sampling and Cut Surface

The used HRS bricks were sampled near the coke side in the coke chamber.

The cut surface photographs are shown in Fig.1. The missing part on the top side of a brick did not fall off during operating time, but during cooling for dismantling the chamber wall. No bricks had damage on the flue chamber side and had little damage on the coke chamber side, although the bricks almost kept their original shape. The difference in damage among the bricks caused by secular changes was small. The remaining parts containing tongue and groove parts other than the damage parts maintained their structures.

The unused HRS brick had transparent coarse grains. However, when checking the whole cut surfaces of the 3, 6.4 and 8 year used bricks, white coarse grains were found to be fairly uniformly dispersed in them. The differ-

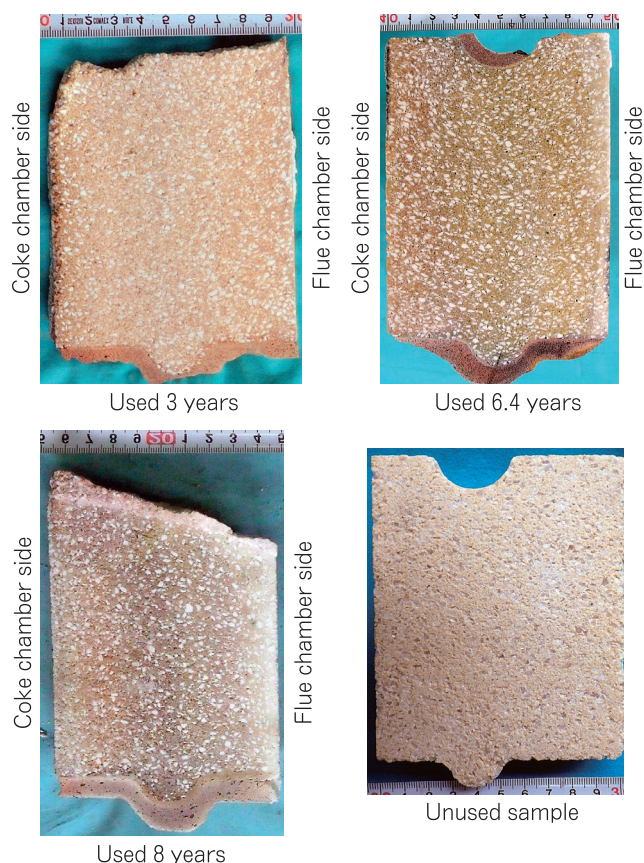


Fig.1 Cut surface of 3, 6.4 and 8 year used hot repairing bricks and an unused hot repairing brick.

3. 特性変化

Fig.2に微量化学組成の経年変化を示す。3年、6.4年は組成の層別差は小さいが、8年ではその差がやや広がっている。この差が色調差にも現れている。しかし、こうした各組成の経年変化は、別項で示した珪石れんがSCDの44年のスケールで見たときの経年変化に比べれば、微小な変化である。後述の鉱物組成変化 (Fig.6)を参考にしたとき、今回の8年程度では、れんが品質に変化を及ぼすほどの成分の侵入はなかったと考えられる。

Fig.3に一般物性の経年変化を示す。やはり、別項の珪石れんがSCDの層別差に比べれば、各年代での層別差は小さい。経年変化の様子は、3年時、6.4年時は未使用HRSれんがに比べ開気孔及び密閉気孔が若干減り、すなわち、緻密質な組織傾向になり、8年時は逆に開気孔、密閉気孔が3年

ence between the used and the unused bricks occurred through the phase transition of silica. The transparent coarse grains disappeared after 3 years or more. Further, the color tone on the cut surface of the 3 year used sample had almost a single tone, the 6.4 year used sample had a little variation in its tone and the 8 year used sample had three tones on the coke chamber side, the center part and the flue chamber side. Accordingly, the samples were divided into three section areas between the coke chamber side and the flue chamber side to investigate the features of the samples.

3. Change of Properties

The secular changes of minor chemical compositions are shown in Fig.2. The difference in chemical compositions among the three layers was small for the 3 and 6.4 year used samples and slightly large for the 8 year used sample. Their differences seemed to be related to the tones. The secular changes of the chemical compositions in the samples were small compared with those of the SCD bricks used on a long term time scale of 44 years. In reference to the changes in mineral phases described later (in Fig.6), the secular changes of the minor chemical compositions were considered to be small because the external compositions, which were enough to produce a change, were not able to penetrate into the 8 year used brick samples in this study.

The secular changes of apparent porosity (AP), bulk specific gravity (BSG) and apparent specific gravity (ASG) are shown in Fig.3. Each difference among the layers per year was smaller than that of the silica brick –SCD– shown in the other report. The 3 year used and the 6.4 year used samples had open and closed pore volumes slightly less than that of the unused HRS brick. That is to say, their textures showed a dense tendency. Conversely, the 8 year used sample had open and closed pore volumes slightly more than that of the 3 year used and the 6.4 year used samples. That is to say, the texture showed a porous tendency. It was impossible to derive general properties

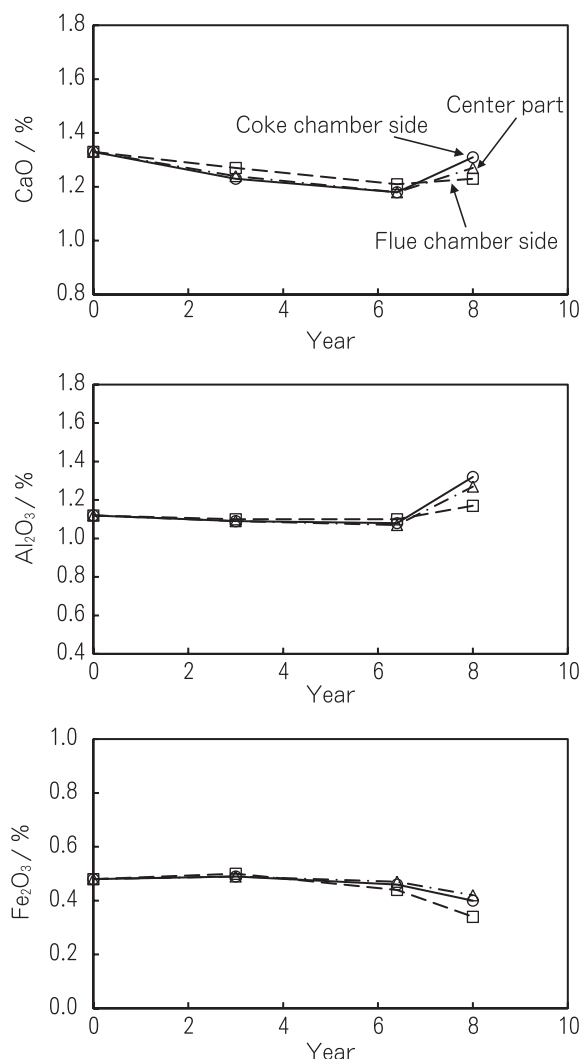


Fig.2 Change in chemical composition.

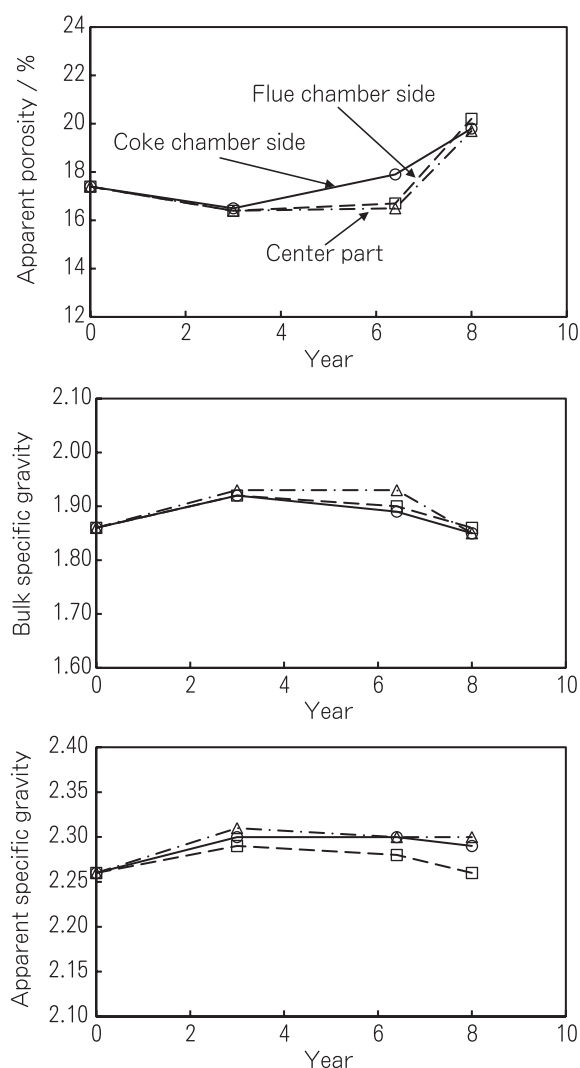


Fig.3 Changes in apparent porosity, bulk specific gravity and apparent specific gravity.

時、6.4年時よりも若干増え、すなわち、多孔質の傾向にある。別項の珪石れんがSCDの一般物性の経年変化の様子と同様に一概には言えないが、8年の短いスパンでの組織変化は、緻密化を経て多孔質に変化しているように見える。今後のAP, BSG, ASGの経年変化の様子に注目したい。

Fig.4に圧縮強度の経年変化を示す。各年代とも未使用HRSれんがよりも高強度であるが、3年目で最も高く、6.4年目、8年目と進むに従い下がる傾向にある。経年のこの傾向は前述の組織の緻密化、多孔質化と対応していると考えられる。今回の層別の差は、別項の圧縮強度の層別の差より大きく、また、燃焼室側の圧縮強度が炭化室側より

from the secular changes of AP, BSG and ASG, although it was similar to the SCD bricks in the other report. However, the used HRS bricks seemed to have a dense texture and then a porous texture in a short span of 8 years. We would like to wait for the results for the secular changes of AP, BSG and ASG after this.

The secular change of the compressive strength is shown in Fig.4. The compressive strength of the used HRS bricks per year was higher than that of the unused HRS brick. In addition, it showed a peak in the 3rd year and was on a declining trend with the passage of 6.4 years, 8 years. This secular change might

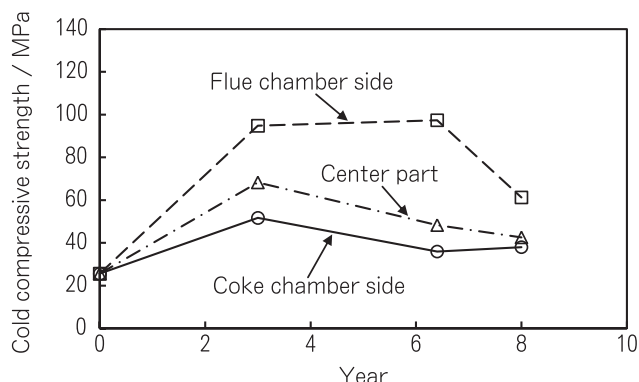


Fig.4 Changes in cold compressive strength.

Table 1 Thermal expansion ratio /% of HRS samples at 1000°C

	3 year used	8 year used	Unused
Coke chamber side	1.20	1.22	1.05
Center part	1.18	1.21	
Flue chamber side	1.18	1.26	

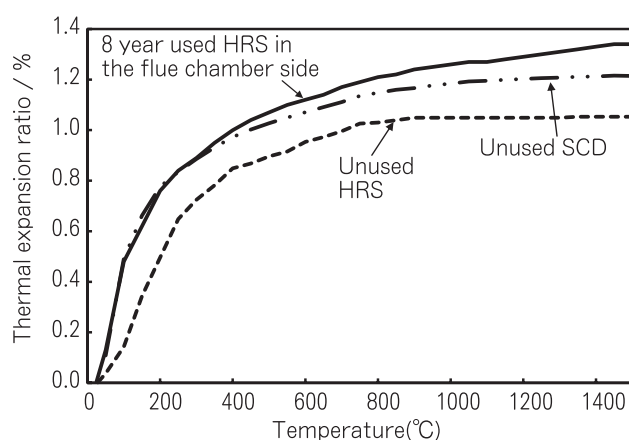


Fig.5 Thermal expansion behavior of 8 year used HRS, unused HRS and unused SCD.

も高い。燃焼室側で強度がもっとも高くなる原因は、Fig.3の一般物性からは説明がつかず、次節で示す微構造と関連づけられる。すなわち、燃焼室側の方の粒間結合が炭化室側よりも進んでいる影響と考えられる。

Table 1に熱膨張率の結果を示す。1000°C熱膨張率は未使用HRSレンガよりも高くなっている。

be related to the dense and porous textures discussed above. Further, the difference in the compressive strength among the layers was larger than that in the other report and also, the compressive strength on the flue chamber side was higher than that on the coke chamber side. However, the AP, BSG and ASG shown in Fig.3 were not able to explain why the compressive strength on the flue chamber side became the highest among the layers. The reason is related to the microstructure described in next section. It was considered that the binding of grains with each other on the flue chamber side progressed more than that on the coke chamber side.

The secular change of the thermal expansion ratio is shown in Table 1. The thermal expansion ratio of the used HRS brick at 1000°C was higher than that of unused HRS bricks. As an example, the thermal expansion behavior of the 8 year used HRS brick is shown in Fig.5. The thermal expansion ratio was higher than that of the conventional silica brick. That result is considered to have been influenced by the microstructure change, especially crystal transition.

4. Change in Microstructure

The secular change in the amount of mineral phase is shown in Fig.6. When the secular change of the mineral phase arose, the crystal phases were only cristobalite and tridymite. The amount of the cristobalite showed a peak height in the 3rd year which was almost the same height in the 6.4th year and 8th year. In addition, the difference among layers was small. On the other hand, the amount of the tridymite on the coke chamber side was almost same as that of the unused HRS bricks, but showed on inclination towards increasing with time on the flue chamber side and the center part. Further, the reason why thermal expansion ratio of the used HRS bricks increased with time, as described in previous section, was that the decrease in the amount of non-crystalline silica and the increase in the amount of tridymite and cristobalite occurred in the unused HRS

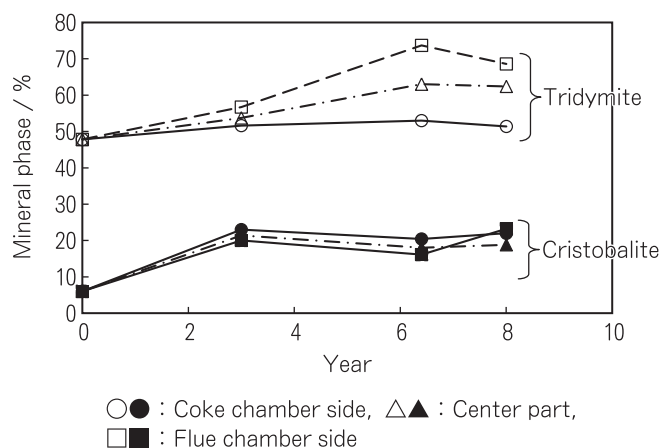


Fig.6 Change in amount of mineral phase.

一例として、8年使用HRSの熱膨張率挙動をFig.5に示す。一般の未使用珪石れんがよりも膨張が大きい。これは後述する微構造変化、特に結晶転移の影響を反映した結果と考えられる。

4. 微構造変化

Fig.6に鉱物組成の変化を示す。経年変化時の結晶相はクリストバライトとトリジマイトである。クリストバライト量は3年時点で増加しているが、6.4年、8年時点でもその量に変化はあまりない。また、層別の差もほとんど生じていない。一方、トリジマイト量は炭化室側では未使用HRSれんがと差はほとんどないが、燃焼室側および中間部で多く、経年とともに多くなる傾向を示す。前述のように、経年により膨張率が高くなるのは、未使用HRSれんがのもつ非晶質シリカが減り、トリジマイト、クリストバライトの結晶相が増えるためであり、特に、トリジマイトよりも熱膨張率の高いクリストバライトが増えているからである⁴⁾。これによりTable 1の大小関係が概ね説明できる。

Fig.7に3年使用HRSの反射電子像を示す。炭化室側、中間部、燃焼室側のいずれの層にもクリストバライトの粗粒が認められるが、各層で異なった微構造を示している。炭化室側では粗粒の形状は概ね整っているが、周縁の一部がマトリックス部の微粒と結合している。中間部は、概ね炭

brick. Another reason was that the cristobalite, with a higher thermal expansion ratio than that of tridymite, increased⁴⁾. Thus, the magnitude relation in Table 1 can mostly be explained.

Reflective electron images of the 3 year used HRS brick are shown in Fig.7. Coarse grains were confirmed in every layer of the coke chamber side, the center part and the flue chamber side. However, every layer had a different microstructure. Coarse grains on the coke chamber side almost had a clear shape, but a part of each peripheral edge region was bound to fine grains in the matrix. The microstructure of the center part was almost similar to that of the coke chamber side. However, the center part was different from the coke chamber side in that the coarse grains in the center part collapsed the shape in each peripheral edge region and the binding of the fine grains progressed into the matrix. The coarse grains, which underwent partial collapse on the flue chamber side, integrated with the matrix through as binding progressed. In other words, when the coarse grains, which were formed from cristobalite, were converted into tridymite, they were micronized and changed to the binding of fine grains with each other. As described in the previous section, the difference in the compressive strength among layers seemed to occur through the changes in microstructure. Namely, the microstructure in the coke chamber side was similar to that of unused bricks and that in the flue side was very different from unused bricks.

Next, pores and low-melting point glass compositions were checked. The pores which showed irregular and rounded shapes had a larger number of open states in the coke chamber side and a larger number of closed states in the coke to flue chamber side. Low-melting point glass compositions seemed to form in the matrix part in the 3rd year.

There were no large difference in microstructure between the 6.4th year and the 8th year. However, there were large differences among the layers each year. On the coke chamber side, it was confirmed that coarse grains were less converted into tridymite phase and there were

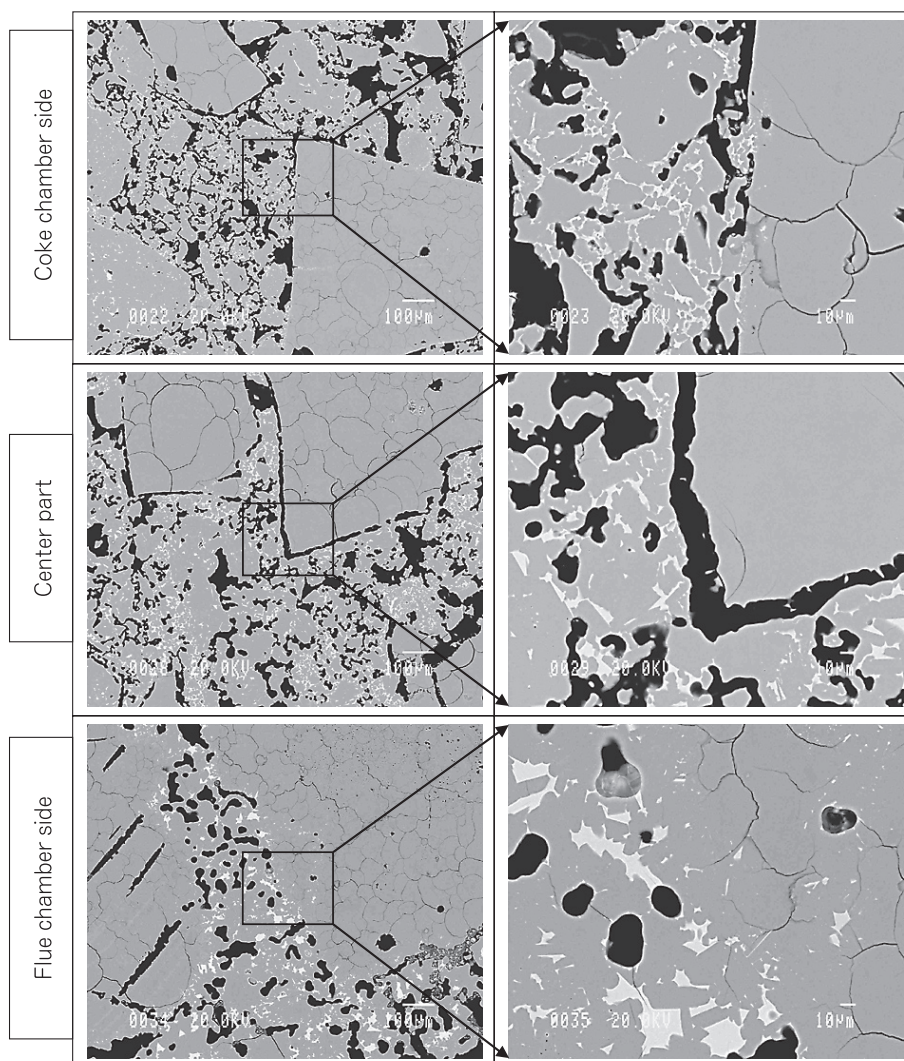


Fig.7 Reflective electron images of 3 year used HRS brick.

化室側に似ている。異なる点は、粗粒の周縁の形状がやや崩れていること、マトリックス部の微粒間で結合が進んでいることである。燃焼室側は粗粒の形状がかなり崩れマトリックスとの結合が進んで一体化されつつある。すなわち、クリストバライトからなる粗粒がトリジマイトへの転移に伴い分解して微粉化し、さらにそれら微粉が結合状態を取りつつあると考えられる。前述の圧縮強度の層別の違いは、このような微構造状態を反映している。すなわち、炭化室側は未使用HRSれんがに近い微構造、燃焼室側は変化が進んだ微構造であり、その違いが層別の圧縮強度差として現れている。

さらに、気孔や低融点組成物（Si-Ca-Al-O系）

many tridymite fine crystals in the matrix parts. In the center part, coarse grains were micronized in the each peripheral edge region and were converted into tridymite phase. On the flue chamber side, the inside area in the coarse grains was well on the way to tridymite phase, too. However, the shape of the coarse grains was maintained in every layer.

It was reported that the texture of the 15 month used HRS bricks was close to that of conventional silica bricks³⁾. The texture on the coke chamber side of every used sample was also similar to that of the conventional silica bricks, as shown in Figs.1 and 7. The texture on the flue chamber side was in a state where coarse grains were being micronized and changed

に注目すると、気孔は炭化室側では開気孔状態のものが多く、燃焼室側に行くに従い、密閉気孔状態のものが増え、しかも不規則ではあるが丸みを帯びた形状になる。低融点組成物は、3年目では主にマトリックス部に認められる。

6.4年目と8年目とで微構造に大きな違いはない。むしろ、層別で違いが生じている。炭化室側は粗粒のトリジマイト結晶への転移は少なく、マトリックス部にトリジマイトの微晶が目立つ。中間部では粗粒周縁部が微粉化したトリジマイトが生じている。燃焼室側は、さらに進んで粗粒内部にもトリジマイト結晶が生じている。しかし、粗粒の形態が存在していることは、いずれの層も変わらない。

HRSの組織は、15ヶ月使用後品で一般珪石れんがのそれに近いものになるとの報告³⁾がある。本使用後試料の炭化室側においても概ねそれに近い様子が見られる(Fig.1, Fig.7)。一方、燃焼室側は、Fig.7に示したように、粗粒の微粉化結合状態の進んだ組織になり、長期使用の一般珪石れんが組織に向かう状態にある。

5. 結び

当社の3年、6.4年、8年使用の熱間補修用特殊珪石れんがHRSの特徴を調べ、以下を知ることができた。

- (1) 切断面のマクロ的な外観では、炭化室面に若干の面損傷が認められるが経年の損傷進展はほとんどなかった。下記の結果も考慮し、実炉で引き続き使用可能と考えられる。
- (2) 未使用HRSれんがの粗粒が経年変化により、非晶質シリカからクリストバライトに変化しているものの、マクロ的状态に変化はなかった。
- (3) 微量化学組成の経年変化は小さく、8年程度では変化を及ばず組成侵入は少なかった。
- (4) 8年の経過の中で、HRSは緻密質あるいは多孔質の組織傾向になり、一概には傾向が現れていない。
- (5) 圧縮強度は未使用HRSれんがよりも高い傾向を示し、また、燃焼室側が高く炭化室側が

to the binding of fine grains with each other, as shown in Fig.7. In the end, that seemed to be developing into the texture of conventional bricks used for a long time.

5. Summary

Hot repairing silica bricks –HRS brand produced by Shinagawa Refractories Co., Ltd.– which were used for 3, 6.4 and 8 years were studied. The following points were clarified.

- (1) Checking the macroscopic appearance of the cut surface, little damage of the samples on the coke chamber side was found and almost did not develop. Considering the results below, continued use may be possible in an actual furnace.
- (2) Coarse grains of unused HRS bricks which were formed from non-crystalline silica were converted to cristobalite phase by the secular change. However, the texture in macroscopic aspects of the texture did not change.
- (3) The secular changes of minor chemical compositions were small and not enough external compositions to produce a change penetrated into the bricks during the short 8 year term.
- (4) The texture of the used HRS bricks became dense and porous in the short span of 8 years. It was impossible to derive the general properties.
- (5) The compressive strength of the used bricks had a tendency to be higher than that of the unused HRS bricks. The used bricks had difference of compressive strengths among the layers showing higher compressive strengths on the flue chamber side and lower strengths on the coke chamber side. There is a possibility that the secular change of the compressive strength depended on not only denseness but also the bonding property of the texture.
- (6) The thermal expansion ratio of the 8 year used HRS bricks was a little higher than that of the unused HRS bricks and unused conventional silica bricks, because of the

低い層別差が生じている。経年による強度の変化は組織の緻密性だけでなく、結合状態も影響している可能性がある。

- (6) 8年使用HRSの熱膨張率は、結晶転移の影響により、未使用HRS、未使用一般珪石れんがよりも若干高かった。
- (7) 鉱物組成の経年変化は組成により異なった。クリストバライトの層別差はほとんどなく、早期に未使用HRSよりも多くなり、以降ほぼ一定量で推移し、トリジマイトは炭化室側で未使用HRSと変わらず、燃焼室側で経年による増加傾向を示した。
- (8) 炭化室側の組織は未使用HRSに近い。燃焼室側は、粗粒形状は一応認められるが、マトリックス部と一体化した微粉化結合状の組織が形成されつつあり、使用中の一般珪石れんがに近づく様子が認められた。

influence of crystalline transition.

- (7) The secular changes of amount of mineral phase were different according to type of mineral phase. The amount of cristobalite with no difference among layers was larger at an early stage than that of unused HRS bricks and had almost a constant value after that. The amount of tridymite on the coke chamber side was almost the same as that of the unused HRS bricks and that on the flue chamber side had a tendency to increase with time.
- (8) The texture on the coke chamber side of the used HRS bricks was close to that of unused HRS bricks. The coarse grains on the flue chamber side were almost confirmed, although the texture was in a state where the coarse grains were being micronized, changed to a binding of fine grains with each other and were being integrated with the matrix. Microstructure of the flue chamber side seemed to get closer to that of conventional silica bricks during use.

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