

炭素含有れんがの荷重下膨張特性

Expansion Under Load Characteristics of Carbon Containing Bricks

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Abstract

The thermal expansion rate under load was measured with a constant load being applied to the sample in order to investigate the volume stability and the state of stress caused by the thermal expansion of refractories under restrained conditions. In this report, we improved the thermal expansion under load measuring method and presumed the amount of elastic and plastic deformation at high temperature for various carbon containing bricks. The results of the measurements were related to the damage behavior of these bricks in actual furnaces.

1. はじめに

耐火物の熱膨張率挙動を評価する上で、自由空間での熱膨張率に加えて、荷重下での膨張率を測定する方法が行われている¹⁾。この荷重下膨張率は、熱風炉の蓄熱室に使用されるチェッカーれんがのように、積み重ねて使用され自重がかかる場合のライニング設計だけでなく、熱間でフレキシブルな力学的挙動を示す耐火物の材料特性の評価にも有効である。通常、荷重下膨張率は室温から目的温度域まで一定荷重の下で測定され、与えられた荷重により試料は変形し、その変形は弾性的変形と塑性的変形の合計であると考えられる。従って荷重下膨張率は、次の式により表わされる。

荷重下膨張率(T, σ) = 膨張率(T) - { Σ (温度 T までの各温度各荷重での塑性変形量) + σ / 弾性率(T)}

つまり、荷重下膨張率は無荷重の熱膨張率からその試料に生じた全ての変形を差し引いた値に等

1. Introduction

Thermal expansion is one of the important characteristics of refractories. In addition to the thermal expansion in free space, the thermal expansion under load has also been measured in order to examine the characteristics of refractories at high temperature¹⁾. The thermal expansion rate under load is useful not only for designing a brick lining stressed by the self load of bricks such as checker brick lining of the regenerator in hot-blast stoves, but also the evaluation of flexible mechanical behavior of refractory materials at high temperature. Conventionally, the thermal expansion rate under load has been measured under a constant load from room temperature to target temperature. The sample expands with the increase in temperature and deforms by a given load at the same time. In this deformation, both of the elastic and plastic deformations are included. Therefore, the thermal expansion rate under

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しいと考えられる。

従来の測定方法では塑性変形と弾性変形が区別されていないが、実炉におけるレンガの目地損傷などを考慮する場合においては、この2種類の変形を区別して考えることが必要であると考えられる。例えば、所定の温度でその変形が全て塑性的な変形であった場合、温度が下がり始めた時点で目地開きが始まり目地損傷を起すと考えられる。これに対し、所定の温度で弾性的変形を有している場合は、温度が下がり始めても直ぐには目地は開かず、ある温度まで下がった時点で目地が開き始めると推測される²⁾。本報告では昇温途中で荷重を負荷・開放することにより、各種炭素含有レンガ（MgO-C, Al₂O₃-SiC-C, Al₂O₃-MgO-C）の高温域での弾性変形量と塑性変形量を区別して評価することを試みた。

2. 実験方法

実験は従来の荷重下膨張測定装置を昇温途中で荷重を増減できるように改良して実施した。試料の酸化を防ぐためN₂ガス雰囲気とし、昇温は室温から1500℃まで5℃/minで実施した。

実炉において予想される荷重条件をFig. 1で説

load can be expressed by the following expression.

Thermal expansion rate under load (T, σ) = Thermal expansion rate (T) - $\{\Sigma(\text{Amount of plastic deformation at each temperature and each load up to temperature } T) + \sigma / \text{Elastic modulus } (T)\}$

In other words, the thermal expansion rate under load is thought to be equal to the value which is the amount of all deformations under load subtracted from the thermal expansion rate without load.

With the conventional thermal expansion under load measuring method, the plastic and elastic deformations could not be distinguished from each other. However, it is necessary to distinguish these deformations in order to consider the joint damage of a brick lining. For example, if deformation of bricks is composed of only plastic deformation at a particular temperature, the joint opening would start at the same time of the decrease in temperature. On the other hand, if elastic deformation is also included in the brick deformation, the joint would not begin to open with the decrease in temperature, and would not start to occur until the elastic deformation ceased²⁾. Therefore, we have attempted

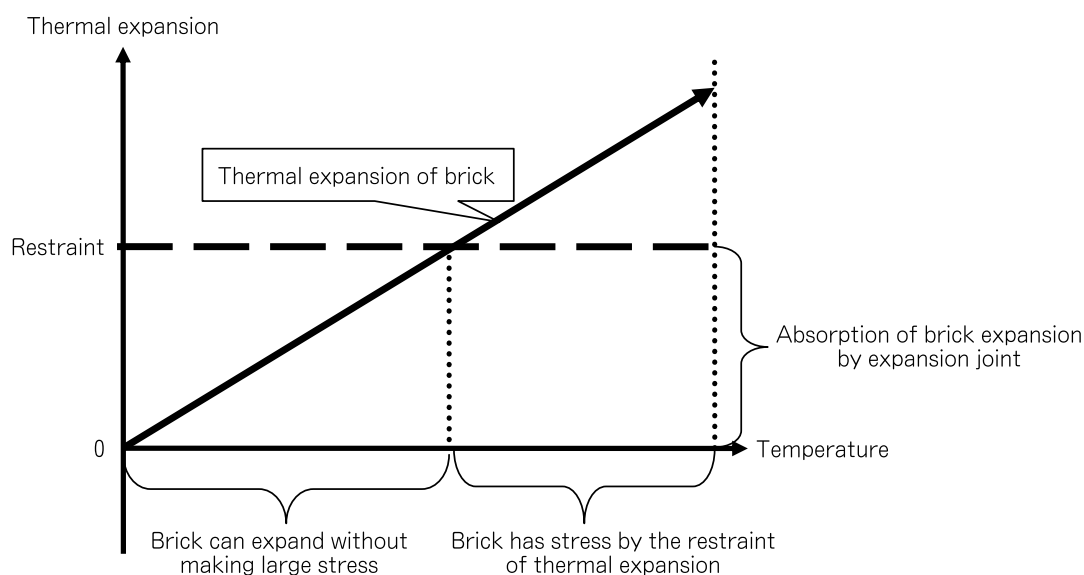


Fig. 1 Image of brick expansion condition in actual furnace.

Table 1 Load condition of each experiment A and B

	Room temp.-999℃	1000-1494℃	1495-1500℃
Experiment A	0.1MPa		
Experiment B	0.1MPa	1.0(0.4*)MPa	0.1MPa

* Al_2O_3 -SiC-C samples are measured at 0.4MPa.

Table 2 Composition of MgO-C samples

Sample		MC1	MC2	MC3
Chemical Composition / mass%	MgO C	85 15		
Binder		Phenol resin	Special binder A	Special binder B

明する。実炉においては目地による膨張吸収により低温域ではあまり大きな応力は掛からない。しかしある温度以上では、膨張吸収量を超えてれんがが膨張し、拘束力が働くようになる。この拘束力は温度が上昇するほど大きくなる。

今回の実験では、装置の制約もあり、膨張吸収代が有効な状態では0.1MPaの荷重、拘束が働く高温では1.0MPaの荷重を与えて測定を行った。測定条件をTable 1に示す。低温域と高温域の境界温度は実炉の条件により異なると考えられるが、本実験では1000℃を境界温度と仮定した。また、1495℃で荷重を1.0(Al_2O_3 -SiC-Cの場合は0.4)MPaから0.1MPaに低減し、弾性による変形の戻りを調査した。

3. 実験結果

3.1 MgO-Cれんがの変形特性

Table 2に示す3種類のMgO-Cれんがについて測定した結果をFigs. 2～4に示す。なお、実験A、Bの誤差を修正するため、実験Aの999℃における膨張率を実験Bの膨張率と等しくなるように補正を行った。この補正は以降の他種れんがについても同様に実施した。これらの測定結果から、本報告における弾性変形量と塑性変形量はそれぞれ以下のように推定した。

to separate the elastic and plastic deformations in the thermal expansion under load by improving the measuring method. This paper describes the evaluation results for various carbon containing bricks (MgO-C, Al_2O_3 -SiC-C, Al_2O_3 -MgO-C) by the new method of thermal expansion measurement under load.

2. Experimental Procedure

The experimental apparatus was improved to enable increasing and decreasing the load during measurement. The test was carried out under an N_2 atmosphere, and the temperature was raised at 5℃/min from room temperature to 1500℃.

Fig. 1 is an image of what brick expansion conditions are thought to be like in actual furnaces. Bricks are thought to be able to expand without creating large stress during low temperatures due to the expansion absorption by the joint. However, the bricks create large stress above a certain temperature, because the thermal expansion of bricks exceeds the expansion absorption and the bricks are restrained. And this stress becomes larger with temperature increase.

In the improved experiment of thermal expansion under load, the load was changed some times during the experiment. The test sample was loaded with the stress value of 0.1MPa to represent a not restrained condition

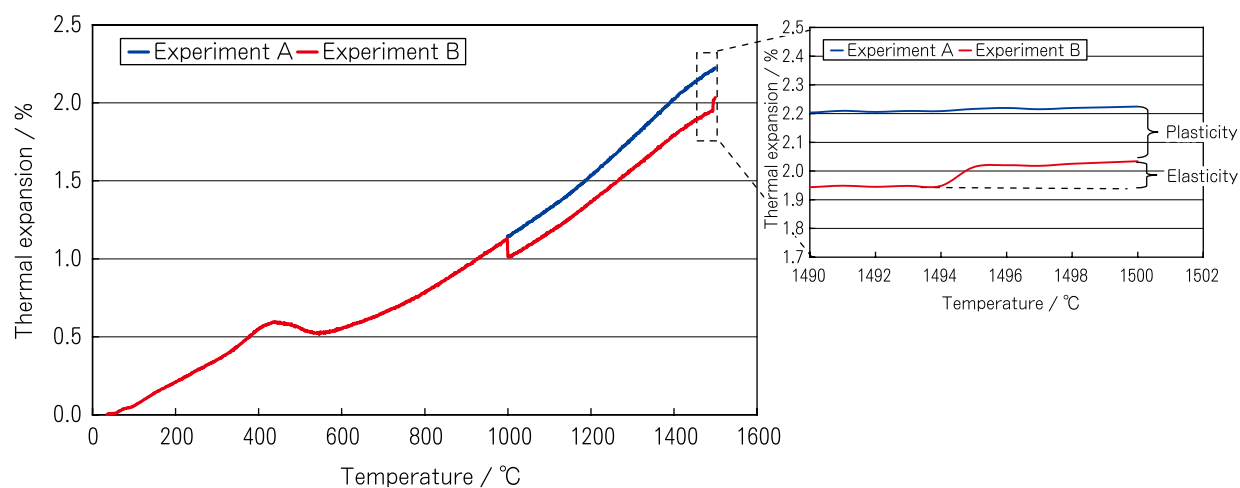


Fig. 2 Thermal expansion curves of MC1.

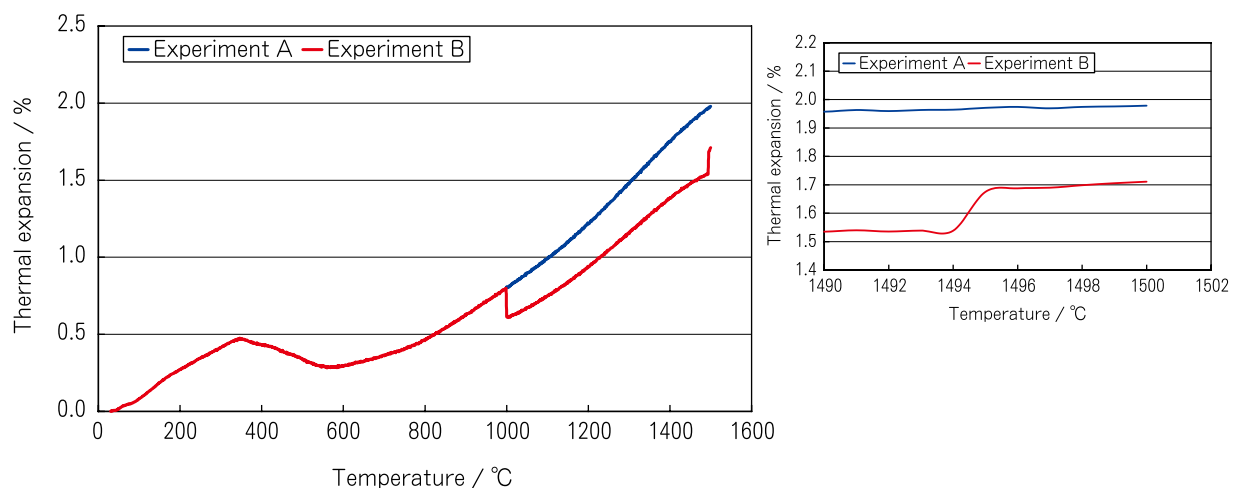


Fig. 3 Thermal expansion curves of MC2.

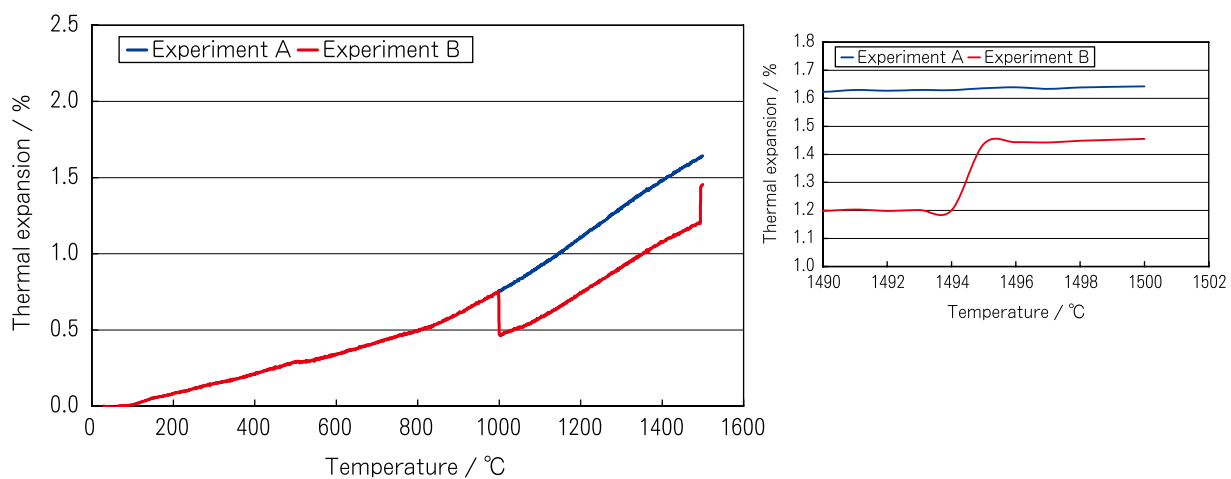


Fig. 4 Thermal expansion curves of MC3.

＜弾性変形量＞

試料が弾性変形を有していた場合、実験Bにおいては1495℃で荷重を低減した際に弾性変形量の分だけ膨張が生じると考えられる。従って、荷重解放後（1500℃）における膨張率から荷重開放直前（1494℃）の膨張率を差し引いた値を弾性変形量と推定した。

＜塑性変形量＞

先に述べたように、荷重下膨張率はある温度の無荷重下の熱膨張率から塑性変形量の累計とその温度における弾性変形量を差し引いた値に等しいと考えられる。そこで、実験Aで測定した曲線の1500℃における膨張率から、実験Bの1500℃荷重開放後の膨張率を引いた値を塑性変形量の累計と推定した。

本実験に用いたMC1はフェノール樹脂をバインダーに用いたMgO-Cれんがであり、主に転炉用・取鍋用れんがとして使用されている一般的なMgO-Cれんがである。MC2は当社が開発した低膨張性MgO-Cれんが³⁾であり、特殊なバインダーを使用することなどでれんが組織を改良し、荷重下で低膨張率を示すMgO-Cれんがである。MC3は受熱後にれんが内に微細気孔を生じる効果のある特殊な有機系バインダーを使用したれんが⁴⁾であり、主に鍋用れんがとして使用されている。

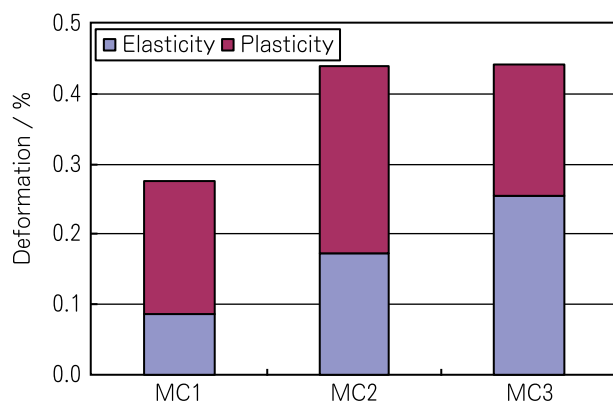


Fig. 5 Elastic and plastic deformation of MgO-C samples.

at low temperature in an actual furnace and a stress value of 1.0MPa to represent a restrained condition at high temperature. Table 1 shows the experimental conditions. In these load changing experiments, the boundary temperature between the low and the high temperature was assumed to be 1000℃ though that value varies in actual furnaces. Moreover, the load was decreased from 1.0MPa to 0.1MPa at 1495℃ (in the case of $\text{Al}_2\text{O}_3\text{-SiC-C}$, the load was decreased from 0.4MPa to 0.1MPa.), in order to measure the elastic deformation.

3. Experimental Result

3. 1 Deformation characteristics of MgO-C brick

Figs. 2~4 show the results for the MgO-C bricks shown in Table 2. The data of experiment A was corrected to accord with experiment B at 999℃, in order to correct for the error margin in experiments A and B. This correction was executed for the other experiments as well. The amount of the elastic deformation and plastic deformation were presumed to be as follows.

＜Elastic deformation＞

After the load was decreased at 1495℃ in experiment B, the sample is thought to have expanded corresponding to its elastic deformation at that temperature. Therefore, the amount of elastic deformation was presumed to be the value which was the thermal expansion rate just before decreasing the load (at 1494℃) subtracted from the rate just after decreasing the load (at 1500℃) in experiment B.

＜Plastic deformation＞

The thermal expansion under load, as described above, is thought to be equal to the value which is the total of the cumulative amount of both plastic deformation and elastic deformation at a given temperature subtracted from the thermal expansion rate without load. So, the amount of plastic deformation was presumed to be the value which was the expansion rate at 1500℃ just after the decrease in load in experiment B subtracted from the expansion

Table 3 Composition of Al_2O_3 -SiC-C samples

Sample		ASC1	ASC2
Chemical Composition / mass%	Al_2O_3	79	55
	SiC	7	5
	C	14	10
	SiO_2	—	30
Binder		Phenol resin	

Fig. 5に測定結果から求めた弾性・塑性変形量を示す。MC1と比較しMC2は約2倍、MC3は約3倍の弾性変形量を有していた。また、塑性変形を加えた全変形量もMC2,3の方が大きい結果となった。

実炉における損傷を考えた場合、高温域における変形量が多いほどれんがの膨張により発生する応力が緩和されると予想され、応割れの低減が期待できる。また、高温域における弾性変形量が多いほど冷却時の目地開きが少なくなると推測され²⁾、MC2およびMC3は実炉において応割れや目地開きによる目地損傷の少ない材質であると考えられる。実際、MC2やMC3は実炉適用時に目地損傷の低減効果が確認されている^{3),5)}。

3.2 Al_2O_3 -SiC-Cれんがの変形特性

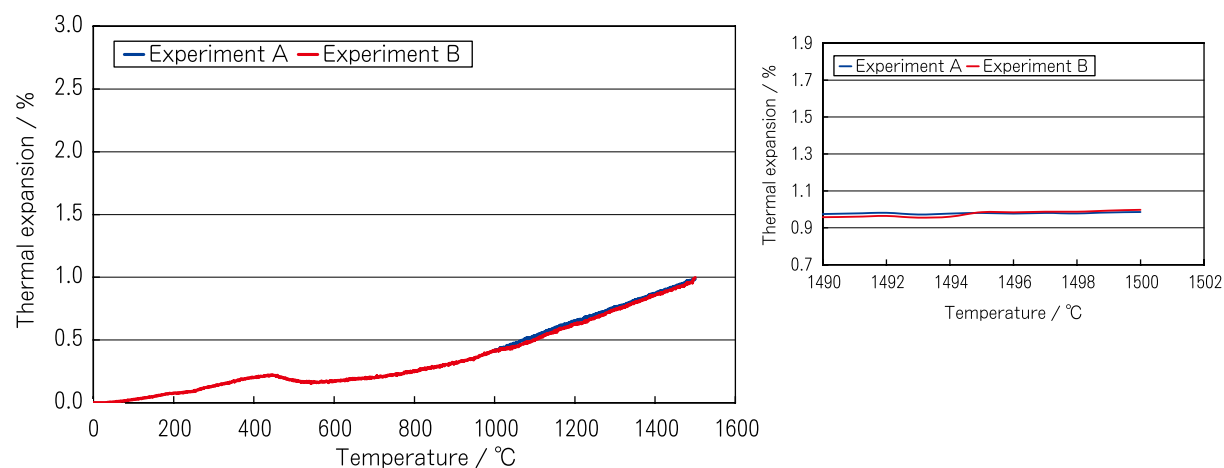
Table 3に示す2種類の Al_2O_3 -SiC-Cれんがについて測定を行った結果をFig. 6, 7に示す。ASC1,2は主に溶銑鍋に使用されている Al_2O_3 -

rate at 1500°C in experiment A.

Three different types of MgO-C bricks were tested (Table 2). MC1, an ordinary MgO-C brick made with phenol resin binder and used for BOF and steel ladles. MC2, a newly developed MgO-C brick with a brick micro structure using a special binder and showing low thermal expansion under load³⁾. And, MC3, another newly developed MgO-C brick for steel ladle-furnaces made with a special organic binder⁴⁾. This special binder resulted in the development of micro pores in the brick matrix after heating.

Fig. 5 shows the measured amount of elastic and plastic deformation obtained from measurements. MC2 and MC3 showed about two times and three times the amount of elastic deformation compared with MC1 respectively. Moreover, the total plastic-elastic deformation values for MC2 and MC3 were larger than that of MC1.

In actual furnaces, bricks which deform at high temperatures are expected to reduce the stress caused by thermal expansion and decrease spalling damage. In addition, joint opening during temperature decrease is expected to be small in bricks which have a large amount of elastic deformation at high temperature. Therefore, MC2 and MC3 are expected to show little joint damage caused by the thermal expansion and

**Fig. 6** Thermal expansion curves of ASC1.

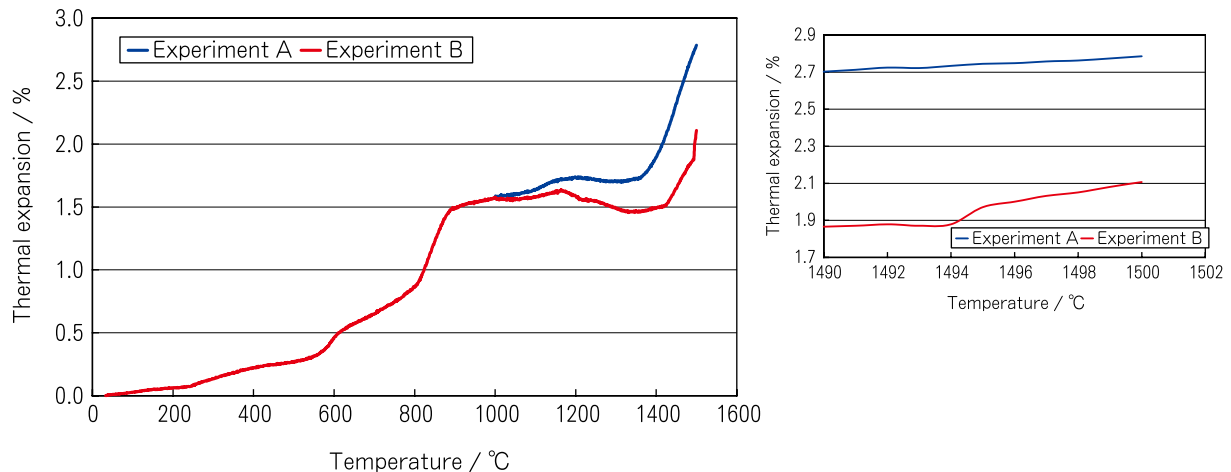


Fig. 7 Thermal expansion curves of ASC2.

SiC-Cれんがであり、ASC2は蠟石を多く含んでいる。蠟石を含むれんがは熱間での変形性に富むため、 Al_2O_3 -SiC-Cれんがでは実験Bで負荷する荷重を0.4MPaとした。

測定の結果、ASC1では塑性変形が確認できず、わずかに弾性変形が見られたのに対し、ASC2は大きな変形を示しており、ASC1と比較し約5倍の弾性変形量を示し、塑性変形も非常に大きな値を示した (Fig. 8)。

蠟石原料の調査結果⁶⁾によると、1000～1100℃の温度域において蠟石に含まれるパイロフィライトからムライトと非晶質シリカが生成し始め、1400℃位からクリストバライトと液相生成による

joint opening in actual furnaces. The decrease in joint damage was observed verified and for both of MC2 and MC3 in actual furnaces^{3), 5)}.

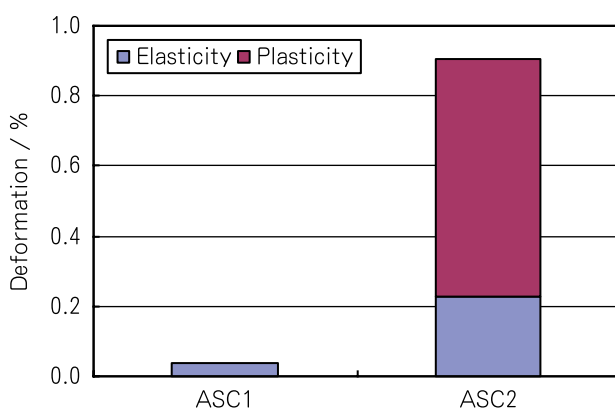
3. 2 Deformation characteristics of Al_2O_3 -SiC brick

Fig. 6 and Fig. 7 show the measured results for the two samples of Al_2O_3 -SiC bricks shown in Table 3. ASC1 and ASC2 are mainly used for hot-metal containers, and ASC2 contains a lot of rouseki material. Because the ASC brick containing a lot of rouseki shows large deformation, the stress after the load increase in experiment B was assumed to be 0.4MPa.

ASC1 shows very little elastic deformation and almost no plastic deformation. On the other hand, ASC2 showed large elastic and plastic deformation, and the elastic deformation was about five times that of ASC1 (Fig. 8).

According to a study⁶⁾ of rouseki raw material, pyrophyllite starts to decompose into mullite and amorphous silica at about 1000～1100℃, and also cristobalite and melt start to generate from the amorphous silica and quarts at about 1400℃. It is estimated that these characteristics of rouseki cause the large deformation at high temperature to ASC2.

Fig. 9 shows the in-furnace appearance of ASC1 and ASC2. ASC1 was observed to have large joint damage. On the other hand, the joint damage was greatly suppressed in ASC2.

Fig. 8 Elastic and plastic deformation of Al_2O_3 -SiC-C samples.

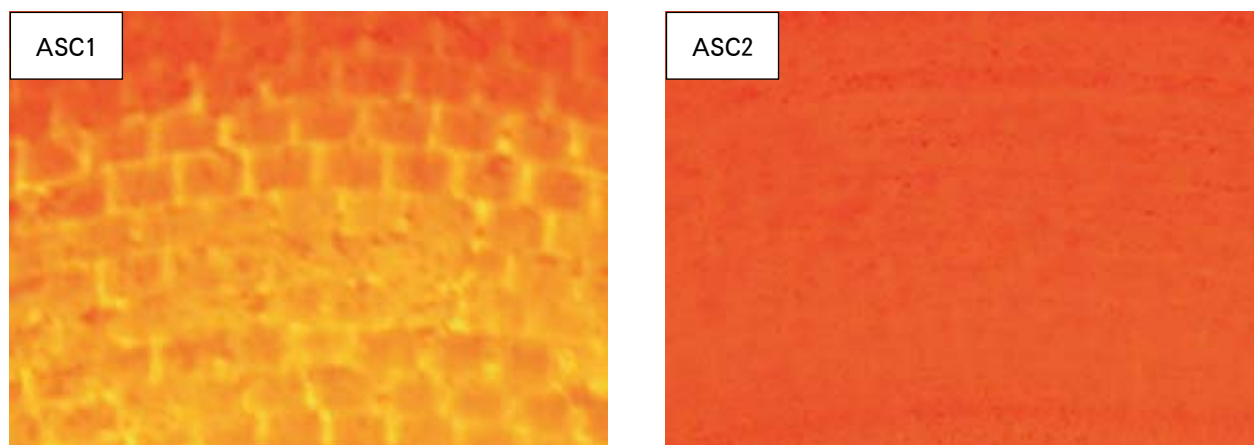


Fig. 9 Appearances of ASC1 and ASC2 in actual furnaces.

急激な膨張が生じるとされている。このことから、蠟石を多く含むASC2は、高温域において蠟石に起因する液相などが生成することで大きな変形能を示していると考えられる。

ASC1およびASC2を実炉へ適用した際の写真をFig. 9に示す。ASC1はれんがの目地が明瞭に認識でき、目地損傷が進行している。一方、ASC2はれんが目地がほとんど認識されず、目地損傷が大幅に改善されている。

以上の結果からも、高温域において大きく変形可能であり、かつ、弾性変形量も多い材質は、実炉における目地損傷に対して有効であることがうかがえる。

3. 3 Al_2O_3 -MgO-Cれんがの変形特性

Table 4に示す Al_2O_3 -MgO-Cれんがについて測定を行った結果をFig. 10, 11に示す。前述のMgO-Cれんがと同様に、AMC1はバインダーにフェノール樹脂を用い、AMC2は微細気孔を生じる特殊バインダー（MC3と同じバインダー）を使用した。AMC2はAMC1と比較し、約2倍程度の弾性変形量を示しており（Fig. 12）、全変形量も大きく、MgO-Cれんがの場合と同様に特殊有機バインダーを用いた方が実炉目地損傷に対して有効であることが示唆される結果となった。

Table 4 Composition of Al_2O_3 -MgO-C samples

Sample		AMC1	AMC2
Chemical Composition / mass%	Al_2O_3	75	
	MgO	10	
	C	15	
Binder		Phenol resin	Special binder B

From the above results, it was confirmed that bricks that are able to deform largely and with large elastic deformation at high temperature can decrease joint damage in actual furnaces.

3. 3 Deformation characteristics of Al_2O_3 -MgO-C brick

Fig. 10 and Fig. 11 show the measured results for the two samples of Al_2O_3 -MgO-C bricks shown in Table 4. AMC1 was made using phenol resin binder. AMC2 was made using a special organic system binder (the same binder as MC3). AMC2 showed about twice the amount of elastic deformation of AMC1 (Fig. 12) and also had large plastic deformation. It was suggested that the special organic binder was also effective for decreasing the joint damage of Al_2O_3 -MgO-C bricks as well as MgO-C bricks.

4. Consideration

From the results of above experiments, it is thought that the binder greatly contributes to the deformation characteristic of carbon

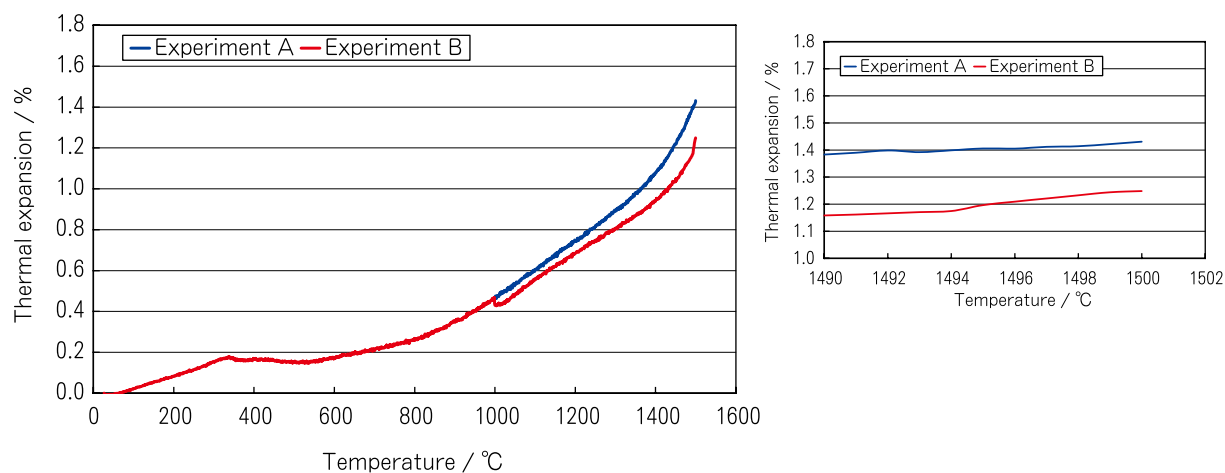


Fig. 10 Thermal expansion curves of AMC1.

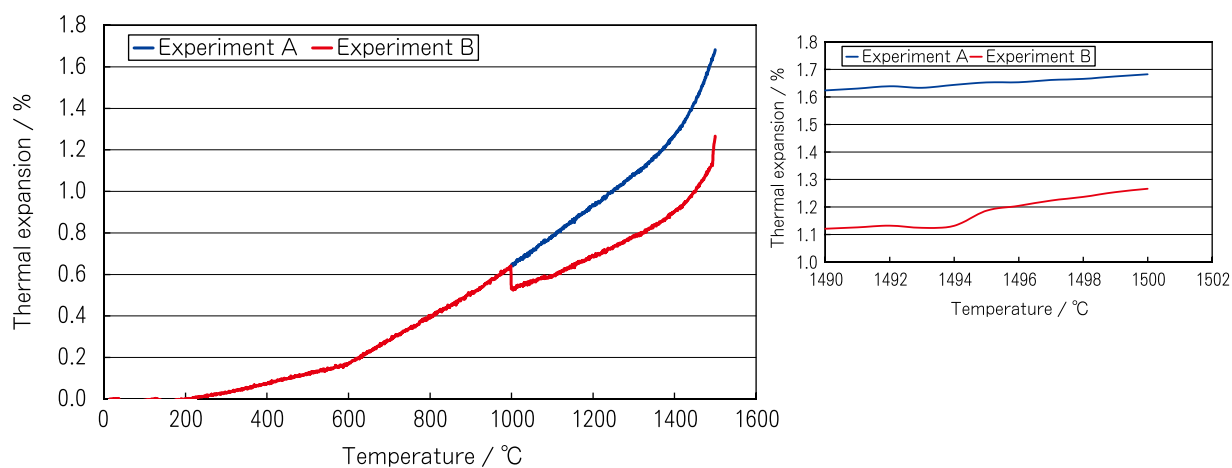


Fig. 11 Thermal expansion curves of AMC2.

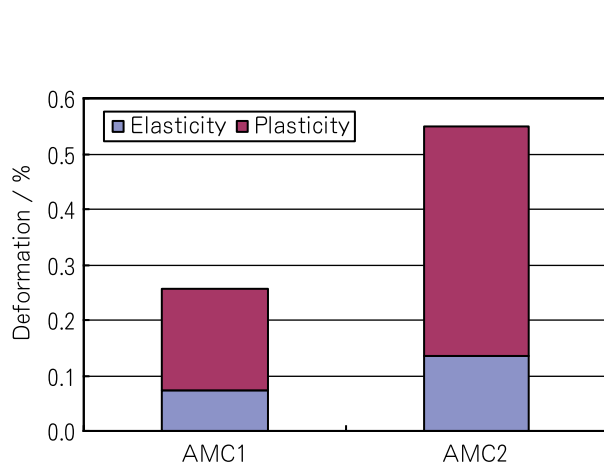
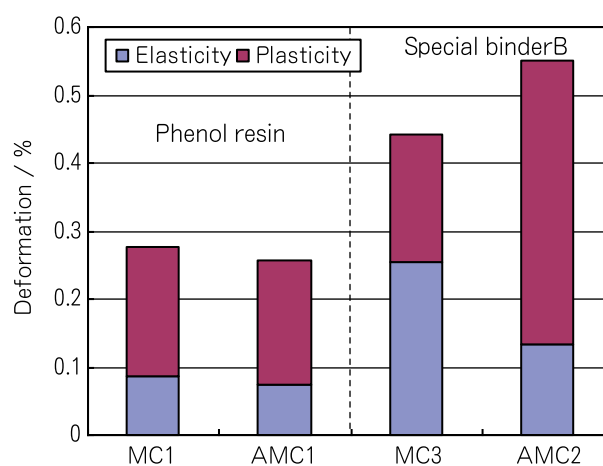
Fig. 12 Elastic and plastic deformation of $\text{Al}_2\text{O}_3\text{-MgO-C}$ sample.Fig. 13 Elastic and plastic deformation of MgO-C and $\text{Al}_2\text{O}_3\text{-MgO-C}$ samples.

Table 6 Load condition of experiment C

	Room temp.-1489℃	1490-1494℃	1495-1500℃
Experiment C	0.1MPa	1.0MPa	0.1MPa

4. 考察

ここまでの結果より、不焼成である炭素含有れんがの変形特性にはバインダーが大きく寄与していることが示唆される。同じバインダーを用いたMgO-Cれんがと Al_2O_3 -MgO-Cれんがの変形量を比較した結果をFig. 13に示す。バインダーにフェノール樹脂を用いた試料では、MgO-Cと Al_2O_3 -MgO-Cれんがは変形量がほぼ同じであり、弾性変形と塑性変形の割合も同程度である。一方、特殊有機バインダーを用いた試料では、いずれの材質もフェノール樹脂の場合よりも大きな変形を示すが、MgO-Cれんがに比較し Al_2O_3 -MgO-Cれんがは塑性変形が大きな割合を示しており、材質の違いによっても変形特性が異なっていることが判る。

このように、炭素含有れんがの高温域での変形特性はバインダーや材質の組み合わせにより異なると考えられるが、荷重履歴（荷重のかかっている温度および時間）の違いによっても変形特性に違いが生じる可能性が考えられる。例えば、室温から高温まで大きな荷重がかかり続ける場合と、高温のわずかな温度域のみ大きな荷重がかかる場合では変形特性に違いが生じると思われる。そこで、 Al_2O_3 -MgO-Cれんがについて1500℃付近の高温域で荷重を増減する条件（Table 6 実験C）で測定を行い、得られた変形量を実験A,Bの場合と比較した。測定結果をFig. 14, 15に示す。なお、弾性変形量は実験A,Bと同様に荷重開放前後の膨張率の差とし、塑性変形量については、荷重を増加する直前（1489℃）の膨張率から荷重を解放した後（1500℃）の膨張率を差し引いた値とした。

測定の結果、AMC1・2ともに実験A, Bで得られ

containing bricks. Fig. 13 compares the amount of deformation of MgO-C bricks with that of Al_2O_3 -MgO-C bricks made with the same binder. In the case of phenol resin binder, the amount of the deformation and the ratio of elastic deformation to plastic deformation of Al_2O_3 -MgO-C brick were almost the same as MgO-C brick. In the case of the special organic binder, the ratio of plastic deformation to elastic deformation of Al_2O_3 -MgO-C brick was different from that of MgO-C brick. This indicates that the deformation characteristic of these bricks depends on not only the type of binder but also the constituent materials.

Thus, it is expected that the deformation characteristic of carbon containing bricks will vary at high temperatures according to the combination of binder and raw materials. On the other hand, the deformation characteristics are thought to vary according to the loading conditions. For example, it is thought that there is a difference in the deformation characteristics between the case of large stress being loaded for a short time at high temperature and that large stress being loaded for a long time from room temperature to high temperature. Therefore, the deformation characteristics were measured under the conditions of the load being increased and decreased in a short period around 1500℃ in order to compare with experiments A and B (experiment C in Table 6). Fig. 14 and Fig. 15 show the results of experiment C for the Al_2O_3 -MgO-C bricks. The amount of elastic deformation was assumed to be the difference between the measured expansion values before and after (at 1494℃ and 1500℃ respectively) decreasing the load, which is similar to the case of experiments A and B. The amount of the plastic deformation was assumed to be the

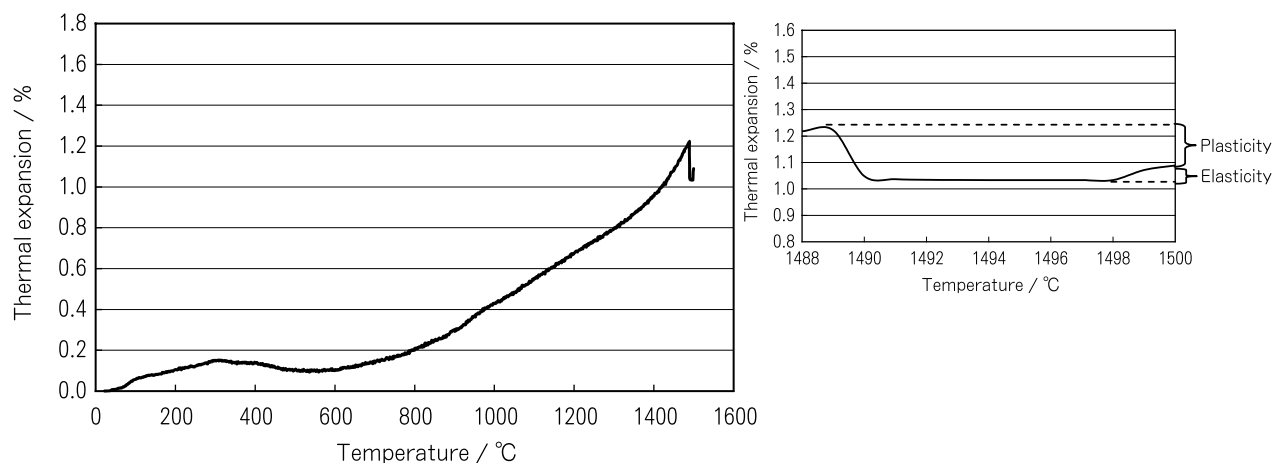


Fig. 14 Thermal expansion curves of AMC1 in experiment C.

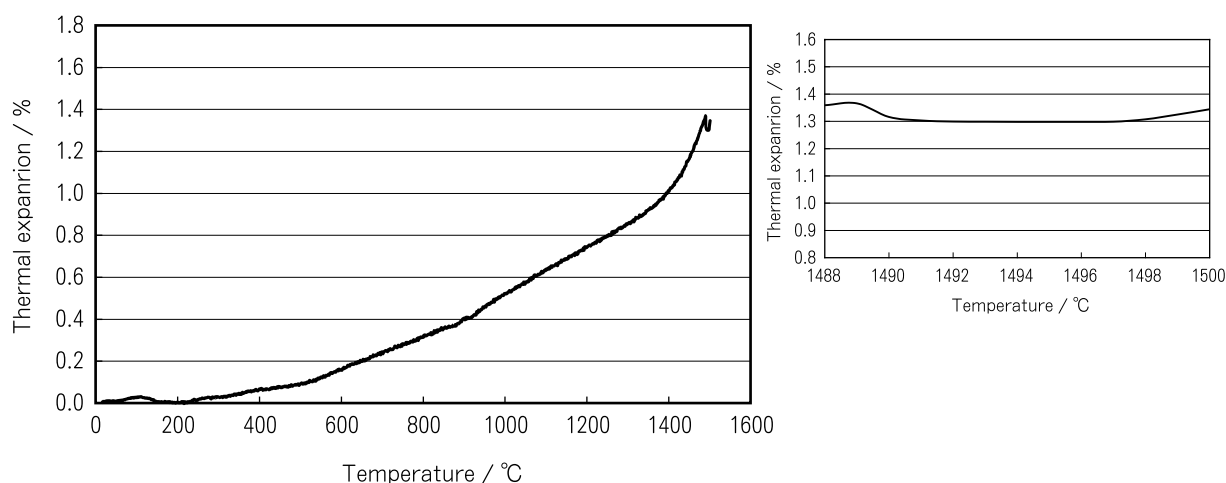
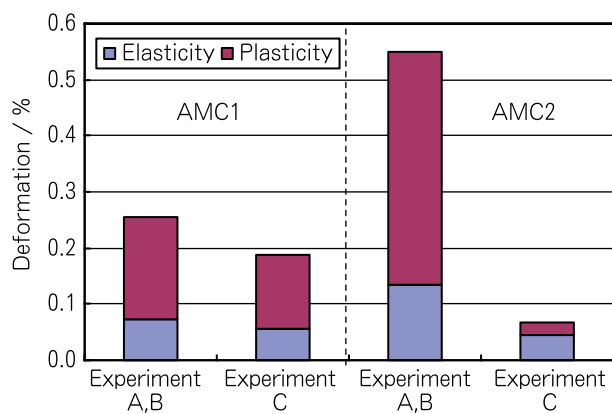


Fig. 15 Thermal expansion curves of AMC2 in experiment C.

Fig. 16 Elastic and plastic deformation of $\text{Al}_2\text{O}_3\text{-MgO-C}$.

value which was the amount of expansion after the load was decreased at 1500°C subtracted from the amount of expansion just before the load was increased at 1489°C.

Both the elastic and plastic deformation in experiment C became small compared with the values in experiments A and B. The amount of the deformation of AMC2 in experiment C, especially, decreased to 1/10 that of experiments A and B (Fig. 16). This suggests that there is a difference in the brick microstructure at high temperature between the case of large stress being loaded from low to high temperature and the case of large stress being loaded only at high temperature. In this way,

た変形量と比較し、実験Cでは弾性・塑性変形ともに変形量が小さくなり、特にAMC2では変形量が実験A、Bの約1/10程度の値となった (Fig. 16)。このことは、低温域から大きな荷重を受けた場合とそうではない場合では、高温域でのれんが組織に違いがあることを示唆していると考えられる。このように、荷重履歴の違いによっても高温域における変形量は変化すると推測され、実炉での状態を調査するには使用条件に近い荷重履歴で測定することが望ましいと考えられる。

5. おわりに

本試験では測定中に荷重を増減させる方法を用いることで、所定の荷重履歴を与えた際の各種炭素含有れんがの高温域における弾性変形量と塑性変形量を推定した。また、得られた結果をもとに、実炉における損傷との関係性について考察を行い以下の知見を得た。

- ①高温域で大きく変形可能であり、なおかつ弾性変形量の大きい材質は迫割れや目地開きの軽減に対して有効と考えられ、実炉においても目地損傷の大幅な改善が見られた。
- ②高温域での変形特性はバインダーや材質の組み合わせにより異なると推測され、さらに、荷重履歴によっても変化すると考えられる。

the deformation characteristic at high temperature varies according to the loading condition too. Therefore, it is preferable to measure the deformation characteristics under similar loading conditions to actual use conditions in order to investigate the deformation state of bricks in actual furnaces.

5. Conclusion

The amount of the elastic and plastic deformation of various carbon containing bricks under certain loading condition was estimated by a new experimental method of thermal expansion under load in which the load was increased and decreased at certain temperatures during measurement. The following are concluded from the results of the experiments for MgO-C, Al₂O₃-MgO-C and Al₂O₃-SiC-C bricks and the damage behavior of these bricks in actual furnaces.

- ①Bricks which are capable of large deformation and moreover have a large amount of elastic deformation at high temperatures are expected to reduce joint damage caused by the thermal expansion and joint opening. In actual furnaces, bricks having such properties have greatly reduced joint damage.
- ②The deformation characteristics of carbon containing bricks are expected to vary at high temperature according to the combination of binder, raw materials, and loading conditions.

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