

SHINAGAWA TECHNICAL REPORT

イソライト工業株式会社
「高耐熱性マイクロポラス系断熱材の
研究」

Isolite Insulating Products Co., Ltd.
“Study of Microporous Insulation Materials
with High Heat Resistance”

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品川技報

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要 旨

1400℃グレードの耐熱性、静止空気並みの低熱伝導率を持ち、加工性、耐水性に優れたマイクロポラス系断熱材を紹介する¹⁾。

従来のマイクロポラス系断熱材は、微細気孔を有することから熱伝導率が低く断熱性に優れる。しかし、高温下ではシリカの結晶化、焼結が進行し気孔が消失するため、耐熱温度は1100℃前後と低く、活用範囲が未だ限定的である²⁻⁴⁾。高耐熱性マイクロポラス系断熱材の開発により、加熱面側での使用が可能となり、熱効率の向上が可能と考えられる⁵⁾。

Abstract

Microporous insulation materials with heat resistance to 1400℃, low thermal conductivity, excellent processability and water resistance was developed¹⁾.

Fine pores give the conventional microporous insulation materials low thermal conductivity and excellent heat insulation. However, the use of the microporous insulation materials was limited due to the crystallization of silica, which lead to the disappearance of the micro pores at about 1100℃²⁻⁴⁾. Because of recent development, microporous insulation materials with high thermal performance can now be used at high temperature places⁵⁾.

1. 緒言

マイクロポラス系断熱材は、微粒子と無機繊維、赤外線散乱材を用いて成形された断熱材である。微細気孔を有することから断熱性に優れ、各種工業炉の炉壁や溶鋼容器などの内張りに使用される。一般的にシリカ系ナノ粒子が使用されるが、高温下で結晶化、焼結し収縮するため、耐熱性が1100℃前後と低く、活用範囲が未だ限定的である。より耐熱性に優れるアルミナ系ナノ粒子を使用しても、1200℃で相転移、焼結が生じ微細気孔

1. Introduction

Microporous insulation materials are mixed with ultrafine particles, inorganic fibers and infrared scattering materials. Due to excellent thermal insulation property, the fine pores can be used at the wall of industrial furnaces and molten steel containers. The use of the silica-based nanoparticles was limited due to crystallization and the shrinkage. Therefore the silica-based microporous insulation materials

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が消失する。そのため、高耐熱性マイクロポーラス系断熱材の開発には収縮の抑制が必要となる。

また、1000℃を超える高温域では、ふく射伝熱が支配的である。Wienの式より、ふく射はマイクロオーダーの波長にピークをもつ光である。ふく射伝熱を抑制するには、この波長の光を散乱させる必要がある。散乱には光の波長と粒径が影響し、光の波長より小さい粒子ではRayleigh散乱、光の波長と同程度の粒子ではMie散乱が生じる。Rayleigh散乱は、散乱光の強度が波長の4乗に反比例する。高温域におけるふく射は赤外線領域の長波長の光であるため、Rayleigh散乱は生じにくい。Mie散乱は波長にほぼ依存せず、散乱強度も大きい。そのため、波長と同程度の粒径の粒を多く含めることで、ふく射を効率よく散乱できる。

以上より、高耐熱性マイクロポーラス系断熱材の開発には、収縮とふく射伝熱の抑制が課題となる。収縮抑制の手法としては骨材の使用が一般的である。本報では、収縮を抑制し、熱伝導率を低減する方法として微細気孔を持つ多孔質材を骨材として使用することを検討した。また、Mie散乱を有効活用するために多孔質骨材の粒径について検討した。

2. 実験

アルミナ系ナノ粒子、赤外線散乱材と無機繊維に多孔質骨材を混合した。多孔質骨材の割合・粒径を変え焼結体を作製した。熱伝導率で断熱性、加熱線収縮率で耐熱性、曲げ強さでハンドリング性、加工性、耐水性を評価した。

2.1 断熱性

多孔質骨材の割合と粒径を変えた試料の熱伝導率を測定した (Fig.1)。横軸は多孔質骨材の割合 (多孔質の重量/ナノ粒子の重量)、縦軸は1000℃における熱伝導率を示す。

骨材を添加していない試料は、収縮をともなった焼結により緻密化し熱伝導率が高い。多孔質骨材を添加することで、熱伝導率は低下し、多孔質骨材の比率が0.2の場合、静止空気並みの熱伝導率を得た。比率が0.2を超えると、熱伝導率が上昇する傾向が見られた。

can only be used as low as 1100℃. Compared with silica-based materials, the thermal resistance of the alumina-based nanoparticles is excellent. However, due to phase transition and the disappearance of the pores at 1200℃, the use of the alumina-based materials was also limited. Therefore, the most important thing in developing highly resistant microporous insulation materials is the suppression of heat shrinkage.

Above 1000℃, the dominate form of heat transfer is radiation. According to the Wien distribution law, radiation is a kind of light with the wavelength at micron order. In order to suppress heat transfer by radiation, it is necessary to scatter the light with the same wavelength of the radiation light. The scattering is influenced by the wavelength of the light and the size of the dielectric materials. The kinds of scattering depend on the size of the dielectric materials and the wavelength. If the dielectric materials are smaller than the wavelength, the scattering is Rayleigh scattering. The opposite is Mie Scattering.

In the case of Rayleigh scattering, the intensity of the scattering light is inversely proportional to the fourth power of the wavelength. The wavelength of radiation at high temperature is in the infrared region, which is much larger than normal dielectric materials. Therefore, Rayleigh is unlikely to happen. Mie scattering is independent of wavelength and scattering intensity is large. To enhance the efficiency of the scattering effect, it is best to put particles with the same wavelength in the dielectric materials.

In summary, the main topic of the development of high heat resistant microporous insulation materials is the control of heat shrinkage and repression of heat transfer by radiation. Normally, heat shrinkage is controlled by adding aggregate to the dielectric. Porous materials with fine pores were used as aggregate to

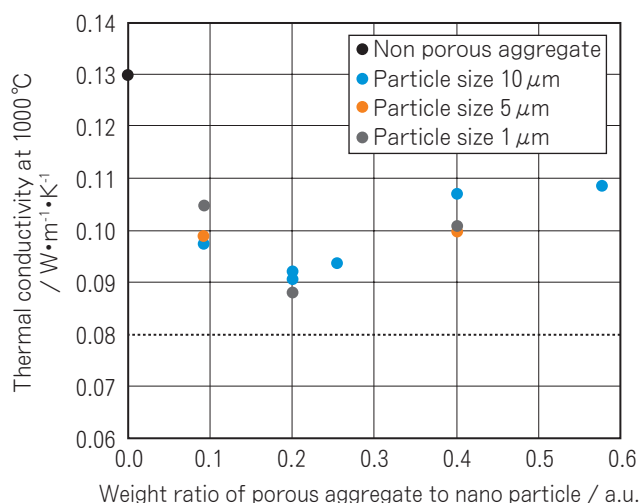


Fig. 1 Changes in thermal conductivity according to particle size and weight ratio of porous aggregate.

Table 1 Changes in pore distribution depend on weight ratio of porous aggregate

Pore diameter / μm	Weight ratio of porous aggregate to nano particle		
	0.1	0.2	0.4
0.5 >	24	26	33
0.5 – 1	24	17	13
1 – 5	33	43	25
5 – 10	14	5	8
10 <	5	9	21

多孔質骨材の粒径に依る熱伝導率への影響は見られなかった。これは、Mie散乱による光の散乱は波長依存性が小さいため、散乱させる波長が厳密に同じである必要はなく、同オーダーであれば広い波長の光の散乱が可能と考えられる。

次に、比率0.1, 0.2, 0.4の試料の気孔径分布を測定した (Table 1)。骨材の増加に伴い $0.5\mu\text{m}$ 以下の微細な気孔が増加したが、同時に $10\mu\text{m}$ 以上の大きな気孔も増加した。骨材比率の増加により、収縮が抑制されナノ粒子が作る微細気孔が維持される。その一方で、骨材同士が作る大きな気孔が増加した。そのため、ふく射の散乱に効率的なミクロンオーダーの骨材が増え、ふく射伝熱は低下、

control heat shrinkage and thermal conductivity. The particle size of the porous aggregate was adjusted to enhance the Mie scattering.

2. Experiment

Alumina-based nanoparticles, infrared scattering material, inorganic fibers and porous aggregate were mixed. The sintered samples were made by changing the ratio of the porous aggregate and the size of the particles. The thermal insulating property, thermal resistance and handling properties were studied by optimizing the thermal conductivity, thermal linear shrinkage and bending strength. The processability and the water resistance were also studied.

2. 1 Thermal insulation

The thermal conductivities of the samples made by changing the ratio of the porous aggregate and the size of the particles was measured (Fig. 1).

The thermal conductivity of the samples without aggregate was high due to the densification caused by thermal linear shrinkage. The thermal conductivity of the samples was reduced by adding the porous aggregate. And the thermal conductivity was as low as the static air when the ratio of the porous aggregate was 0.2. However, the thermal conductivity was increased when the ratio of the porous aggregate was higher than 0.2. There is no relationship between the thermal conductivity and the particle size of the porous aggregate. The light of the thermal radiation in a wide range can be scattered due to the non-strictness relationship between the wavelength and the Mie scattering.

The pore size distribution of the samples (the ratio was 0.1, 0.2 and 0.4) was optimized (Table 1). The ratio of fine pores of less than $0.5\mu\text{m}$ and over $10\mu\text{m}$ was increased by increasing the amount of aggregate. There was no change of fine pores made by the nanoparticles used to suppress the thermal shrinkage even by increasing the ratio of the aggregate.

大きな気孔により対流伝熱は増加し、比率0.2で熱伝導率が極小値をとると考えられる。以降の試験では、多孔質骨材の比率は0.2に固定した。

2. 2 耐熱性

2. 2. 1 最高使用温度

多孔質骨材の粒径を変えて試料を作製し、加熱線収縮率を測定した (Fig.2)。最高使用温度の評価はASTM C 1676-08⁶⁾に基づき、加熱条件は1400℃×24hで行った。粒径の大きな骨材を使用することで、加熱線収縮率は低下した。粒径5μm以上の場合、加熱線収縮率は2%以下となり、耐熱性は1400℃グレードを満たす。

2. 2. 2 常用使用温度

常用使用温度を確認するため、長期加熱試験を実施した (Fig.3)。加熱温度は1300℃、保持時間は最大720hまで連続加熱を行い加熱線収縮率を測

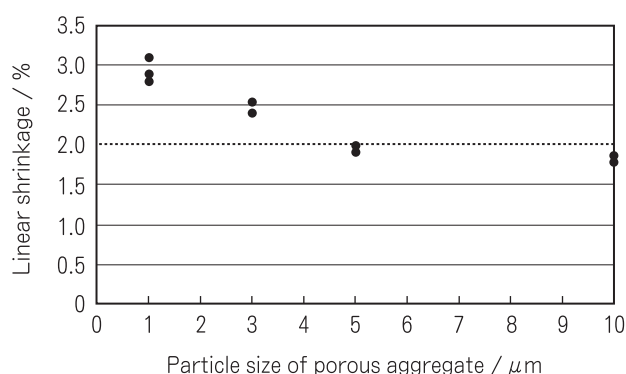


Fig. 2 Changes in linear shrinkage due to particle size of porous aggregate.

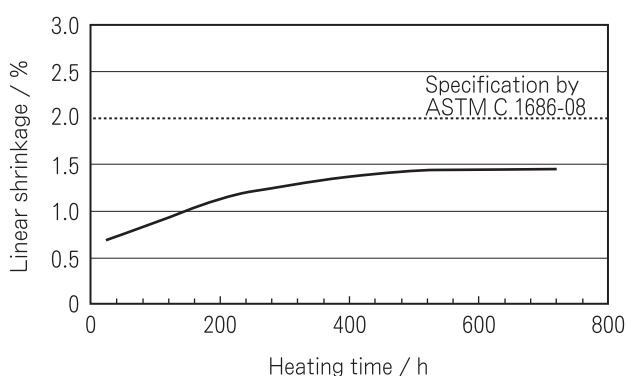


Fig. 3 Changes in linear shrinkage due to heating time at 1300℃.

However, the fine pores that were the same size of the aggregate were increased. Therefore, when the amount of the micron aggregates used to increase of the efficiency of the radiative scattering were increased, the radiative thermal heat was decreased and the convective thermal transfer was increased due to the large pores. The smallest thermal conductivity was optimized when the ratio was 0.2. Therefore, the ratio of the aggregate was fixed at 0.2 in the subsequent tests.

2. 2 Heat resistance

2. 2. 1 Maximum working temperature

The thermal linear shrinkage was optimized by changing the particle size of the porous aggregate (Fig. 2). Based on ASTM C 1676-08⁶⁾, the maximum working temperature was evaluated and the heating condition was 1400℃×24h. The thermal linear shrinkage was decreased by increasing the amount of large particle size aggregate. When the particle size of the aggregate was larger than 5μm, the thermal linear shrinkage was less than 2%. Therefore, the sample has a working temperature as high as 1400℃.

2. 2. 2 Normal working temperature

To confirm the normal working temperature, a long-term heating test was carried out (Fig. 3). The thermal linear shrinkage was tested at a heating temperature of 1300℃ and heating time of 720 h. After heating by 480 h, the thermal linear shrinkage of the sample was 1.5%. Therefore, it is believed that the sample can be used in long-term.

2. 3 Handling property・Processability

The modulus of the rupture of the samples was optimized by adjusting the particle size of the porous aggregate. (Fig. 4).

Because of the particle size of the aggregate was increased, the modulus of rupture was decreased. The modulus of rupture of the porous sample was influence by the bonding strength between the particles. The result of

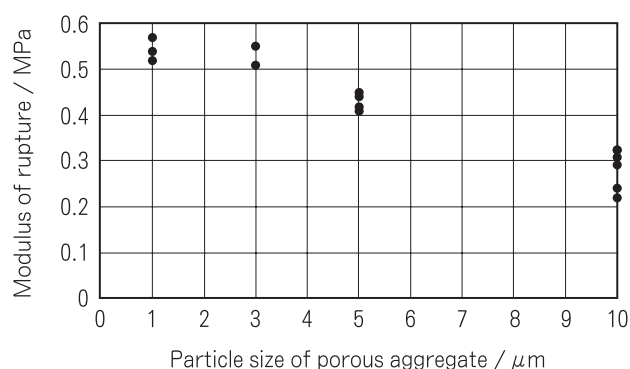


Fig. 4 Changes in modulus of rupture due to particle size.

定した。480h以降、加熱線収縮率は約1.5%で収束している。1300℃での常用が可能と判断される。

2.3 ハンドリング性・加工性

多孔質骨材の粒径を変え、曲げ強さを3点曲げにより測定した (Fig.4)。

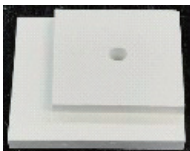
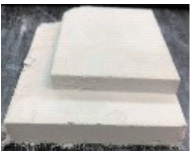
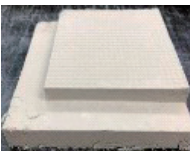
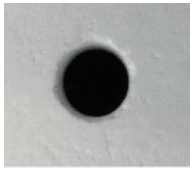
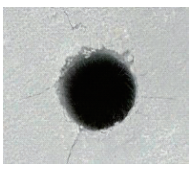
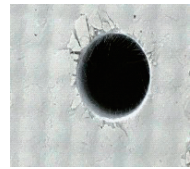
粒径が大きくなるにつれ、曲げ強さは低下した。多孔質体の曲げ強さは、粒子間の結合の強さの影響を受ける。耐熱性の結果から、粒径が大きいほど収縮止めとして機能すると考えられる。粒径が大きいほどナノ粒子間の焼結は進まず、粒子間の結合が弱いと考えられる。

耐熱性が1400℃グレードとなる粒径5 μm では、曲げ強さ0.4MPaとなった。曲げ強さ0.4MPaは、一般的なマイクロポーラス系断熱材の曲げ強さの2倍あり、十分ハンドリングが可能と考え

thermal resistance shows that the thermal linear shrinkage of the sample became smaller when the particle size become larger, which can improve the performance of the samples. However, when the particles size of the aggregate became larger, the sintering between the nanoparticles was stopped. Therefore, the bond the particles became weak. When the particle size of the aggregate was 5 μm , the modulus of rupture of the sample used at 1400℃ was up to 0.4MPa which was 2 times higher than the normal microporous insulation. Therefore, it is believed that handling property is sufficient.

The processability of the samples made by porous aggregates with a particle size of 5 μm was measured (Table 2). The appearance of the samples was observed after being processed by step and drilling. For comparison, normal microporous insulation materials were processed by the same method and were observed. For the step processing test, there was no chipping on the developed samples, which had a clear ridgeline on the surface. And there was no cracking on the samples processed by drilling. Therefore, compared with the normal microporous insulation materials, the processability of the developed samples was excellent.

Table 2 Appearance of samples after processing test

		Developed products	Reference1	Reference2	Reference3
Bulk density / $\text{kg}\cdot\text{m}^{-3}$		407	226	366	251
Processing test	Machining condition 800 $\text{mm}\cdot\text{min}^{-1}$				
	Drilling condition $\phi 10$				

られる。

粒径 $5\mu\text{m}$ の多孔質骨材を使用した試料の加工性評価を行った (Table 2)。段加工および孔加工を行い、外観を評価した。段加工はフライス盤、孔加工はボール盤にて行った。比較試料として、一般的なマイクロポーラス系断熱材についても同様の評価をした。開発品のみ、段加工において、欠けの発生が無く稜線も明瞭に出ている。また、孔加工においてもひび割れの発生が無く、一般的なマイクロポーラス系断熱材と比べ、加工性に優れることがわかる。

2. 4 耐水性

マイクロポーラス系断熱材は、吸水によってラミネーションが生じやすく、また、乾燥時には大きく収縮するため、断熱性の低下が懸念され使用用途が限定される⁷⁾。耐水性評価として水に浸漬し、乾燥後の外観と物性を比較した。具体的には試料を10秒間完全に水中に浸漬させた後、 $100^{\circ}\text{C} \times 24\text{h}$ で乾燥させた。乾燥後に端面の外観および面方向、厚み方向の収縮を確認した (Table 3)。

試験後、一般的なマイクロポーラス系断熱材では、ラミネーションおよび体積収縮が発生した。開発品は、ラミネーションの発生や収縮が無く耐水性に優れていることがわかる。

3. まとめ

多孔質骨材の添加により、焼結による収縮が抑制され、熱伝導率が低下した。多孔質骨材の添加

2. 4 Water resistant

Because of the lamination, the microporous insulation materials absorbed water very easily. After sucking in water, the thermal shrinkage of the samples was high after drying, which limited the use of the samples due to deterioration of the thermal insulation⁷⁾. After immersing for 10 seconds, the appearance and physical properties of the dried samples ($100^{\circ}\text{C} \times 24\text{h}$) were optimized.

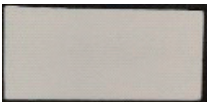
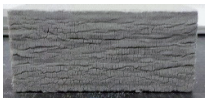
The appearance and thermal shrinkage (plane and thickness direction) of the samples were observed (Table 3).

After the test, the lamination and volume shrinkage of the normal microporous insulation were found. On the contrary, there was no lamination or volume shrinkage in the developed samples, which means the water resistance of the samples was excellent.

3. Summary

By adding the porous aggregate, the thermal shrinkage was suppressed and the thermal conductivity was lowered. The thermal conductivity of the sample became as low as static air by optimized the amount of the porous aggregate. Consistent with the prediction, scattering as a consequence of the micro aggregate was confirmed. When the ratio higher than the optimized value, the number of pores larger

Table 3 Appearance of samples after water resistant test

		Developed products	Reference1	Reference2	Reference3
Appearance	Before test				
	After test				
Shrinkage	Linear shrinkage / %	0.0	2.4	0.9	0.7
	Thickness shrinkage / %	0.0	8.7	3.6	6.6

率を最適値にすることで、静止空気並みの熱伝導率となった。これは、ミクロンオーダーの骨材が、ふく射の散乱に効果的であるとの予測と一致した。一定比率を超えると、 $10\mu\text{m}$ 以上の大きな気孔が増え、対流伝熱が増加し熱伝導率が上昇したと推定できる。

使用する多孔質骨材の粒径は、加熱線収縮率、曲げ強さに影響を与えた。粒径の大きい骨材を使用することで、焼結を抑制する効果は大きくなり、加熱線収縮率は低下する。一方で、焼結を抑制することで曲げ強さは低下するが、適正な粒径の骨材を使用することで、 1400°C グレードの耐熱性と、曲げ強さを両立できることが判った。

作製したマイクロポーラス系断熱材は、加工性、耐水性に優れ、静止空気並みの熱伝導率、 1400°C グレードの耐熱性を持つことから、加熱面で使用でき、省エネに効果的な断熱材としての貢献が期待できる。

than $10\mu\text{m}$ increased. Therefore, the thermal conductivity increased due to the increase in the convective heat transfer.

The thermal linear shrinkage and the modulus of rupture was influenced by the particle size of the porous aggregate. The sintering was suppressed by using the larger aggregate, which leading to the decrease in the thermal linear shrinkage. However, by using the larger aggregate, the modulus of rupture was decreased because of suppressed sintering. Therefore, the thermal resistance and the modulus of rupture could be balanced by using the proper particle size of aggregate.

The processability and water resistance of the fabricated microporous insulation were excellent. The thermal conductivity of the sample was comparable to static air. The developed sample can be used at temperature as high as 1400°C and can be used at the thermal surface in the furnace. Therefore, this insulation materials can be expected to save energy.

References

- 1) T. Miyake, A. Sueyoshi and T. Hashimoto : Taikabutsu, **70** [3] 126 (2018).
- 2) S. Suetake and A. Sueyoshi : Taikabutsu, **69** [3] 148 (2017).
- 3) S. Suetake and A. Sueyoshi : Taikabutsu, **70** [1] 7-10 (2018).
- 4) M. Takahashi, S. Suzuki, T. Kobayashi, and T. Araki : Zairyou, **31** [348] 873-877 (1982).
- 5) H. Sumimura and A. Sueyoshi : Taikabutsu, **68** [6] 245-248 (2016).
- 6) American Standard Test Method, C 1676-08.
- 7) A. Inoue, S. Hosohara and Y. Kiyota : JFE Gihou, [38] 69-74 (2016).