

SHINAGAWA TECHNICAL REPORT

ピッチの諸特性が高炉樋用流し込み材の 特性に与える影響

Influences of Pitch Powder Characteristics on Properties of Castable Refractories for Blast Furnaces Trough

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報文／REPORT

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要 旨

高炉樋用流し込み材には Al_2O_3 -SiC-C材質が使用されており、耐用性向上には熱間での特性が重要とされている。また、それらの特性に影響を及ぼすカーボン原料としてピッチが使用され、ピッチの特性を示す軟化点やQI値に加え β -レンジ量で整理し、高炉樋用流し込み材の熱間強度および耐食性に与える影響を調査した。その結果、 β レジン量と熱間強度および耐食性に高い相関性が認められた。 β -レジンは熱間強度や耐食性に大きく寄与し、ピッチ選定時の重要な指標と考えられる。

Abstract

To realize satisfactory durability of Al_2O_3 -SiC-C castable refractories for blast furnace trough, its physical properties need to be secured at elevated temperatures. Pitch powder is frequently applied as a raw material for carbon component which influences the physical properties of castable refractories. The influences of the characteristics of blended pitch powder, such as softening point, QI value or amount of β -resin, on physical properties of castable refractory bodies were investigated. A high correlation was observed in a series of experiment between the amount of β -resin in blended pitch powder and major physical properties of castable refractories, indicating that the amount of β -resin is one of the important guideposts for selecting pitch powder to be blended in castable refractories for the blast furnace trough.

1. 緒言

長年、高炉樋用流し込み材にはアルミナ、炭化ケイ素、カーボンを主成分とする流し込み材が使用されてきた。なかでもカーボンは流し込み材の強度や耐食性を左右する重要な原料のひとつであるが、カーボン原料としてはピッチが使用されることが多い。ピッチは加熱によって材料中に拡散しカーボンボンドを形成する(Fig.1)。このカーボンボンドの形成により、強度や耐食性といった材料特性の向上が期待される。

1. Introduction

Monolithic refractories composed of alumina, silicon carbide and carbon have been used as castable for blast furnace trough refractories for many years. Pitch powder is frequently blended in castable refractories as carbon component raw material. It is one of the important components which influences the mechanical strength and corrosion resistance of blast furnace trough refractories. As schematically illustrated in Fig. 1, blended pitch is diffused into the

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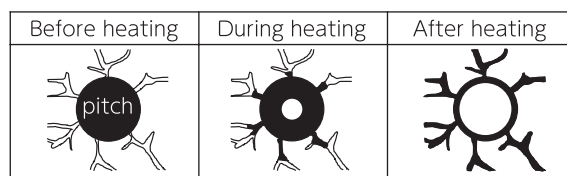


Fig. 1 Schematic illustration for carbon bonding formation by diffused pitch ingredients.

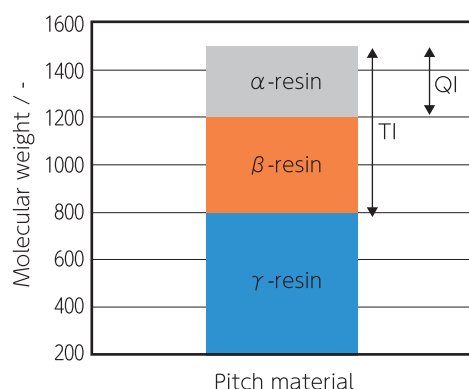


Fig. 2 Ingredient compositions of pitch.

これまで、ピッチ種が耐火物の特性にどのような影響を与えるかについて調査された例は多数あるが、そのほとんどがピッチの軟化点に着目した内容であった^{1,2)}。これは、軟化点と材料特性に相関が見られる場合が多いからである。しかし、鈴木らは軟化点では整理できない場合があり、ピッチのQI値と材料の熱間強度や耐食性に相関があると報告している³⁾。

Fig.2は、溶剤分別によるピッチの成分組成の分類を示している。ピッチは、キノリン不溶分(QI、 α -レジン成分)、トルエン不溶分(TI)を測定することで分子量ごとに分けられ、QIは分子量が1200以上の成分、TIは分子量が800以上の成分を示している⁴⁾。

また、 β レジンにはキノリンに可溶で、トルエンに不溶な成分で、下記の式で示すように、 β レジン量はQI値とTI値の差分で算出される。

$$\beta \text{ レジン量 (mass\%)} = \text{TI (mass\%)} - \text{QI (mass\%)}$$

この成分はピッチに粘りを与えること、さらに炭化時に強い粘結性を示すことが知られている。黒田によれば、 β -レジンにはピッチの結合成分を担っていると報告されており⁵⁾、高炉通用流し込み材の材料特性に影響を与えている可能性が考えられるが、 β -レジンが流し込み材の材料特性に与える影響について報告された例は少ない。

そこで本研究では、ピッチ特性として軟化点やQIに加え

refractory body by heating and forms high-strength carbon bonding which contributes to improvement of refractory properties, such as physical strength and corrosion resistance.

There have been many reports in which the influences of pitch type on refractory properties were investigated by mainly focusing on the softening point of pitch^{1,2)}. The major reason for taking up the softening point of pitch was that a strong relation was observed between the softening point of pitch and refractory properties in many of the investigated results. Suzuki et al. pointed out, however, that some of the investigation results cannot be explained by the softening point of pitch and correlation between QI (quinoline insoluble) value and refractory properties such as mechanical strength at elevated temperatures and corrosion resistance³⁾.

Fig. 2 shows ingredient compositions of pitch classified by solvent fractionation. By measuring the QI (quinoline insoluble or α -resin) and TI (toluene insoluble) values, the ingredient compositions contained in pitch powder are separable in concordance with molecular weight. QI and TI are pitch compositions with molecular weights of over 1200 and 800, respectively⁴⁾. As per Fig. 2, amount of β -resin, another pitch composition which is soluble into quinoline but insoluble into toluene, can be calculated by subtracting QI value from TI value.

$$\text{Amount of } \beta\text{-resin (mass\%)} =$$

$$\text{TI value (mass\%)} - \text{QI value (mass\%)}$$

It is known that β -resin imparts viscosity to pitch and creates a strong caking property by carbonization. Taking into account the peculiar characteristic of β -resin reported by Kuroda⁵⁾, of β -resin playing an important role in bonding formation, it was thought that the amount of β -resin in pitch powder would influence properties of castable refractory for blast furnace trough. However, there are few reports on this issue, namely, the influences of β -resin in pitch

Table 1 Properties of pitch powders

	A200	A250	A300	B	C
Softening point / °C	200	250	300	235	280
Fixed carbon / mass%	77	80	83	83	80
QI / mass%	24	42	51	11	23
TI / mass%	53	65	72	49	70
β -resin / mass%	29	23	21	38	47

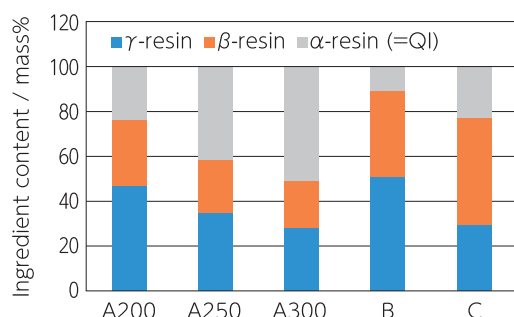


Fig. 3 Comparison of ingredient proportions in each pitch powder.

て β -レジンにも着目し、ピッチの諸特性が高炉樋用流し込み材の特性に与える影響について調査した。

2. 試験方法

2. 1 使用したピッチの特性

Table 1に今回使用したピッチの特性を示す。ピッチAは出発原料が同一で熱処理により軟化点を变化させたピッチである。Aの後に続く数値は軟化点を示している。ピッチB、ピッチCはそれぞれ出発原料や製造方法が異なるピッチである。Fig.3に各ピッチの β 、 γ -レジン量およびQI値を示す。ピッチAは軟化点が上昇するほどQI値が高く、 β -レジン量は低くなる。ピッチBは全ピッチ中で最もQI値が低く、ピッチAよりも β -レジン量が多い。ピッチCは、ピッチA200と同等のQI値を持ち、全ピッチ中で最も β -レジン量が多い。

2. 2 供試配合

Table 2に試験配合を示す。 Al_2O_3 -SiC-Cの配合をベースとし、ピッチの種類及び添加量を変化させた。カーボン含有量の違いによって材料特性が変化しないようにするた

powder on the properties of blast furnace trough refractories. In this regard, focusing on the amount of β -resin contained in pitch powder as well as on the softening point and QI value of pitch, the influences of the characteristics of blended pitch powder on the properties of castable refractories for the blast furnace trough were investigated.

2. Experiment

2. 1 Characteristics of blended pitch powder

The characteristics of the pitch powder used for the experiment are summarized in Table 1. Three types of A series pitch powder were prepared from an identical starting raw material with varying heat treatment, softening points which are indicated by numeric values after A. Pitch powders B and C were prepared from different starting raw materials by different fabrication methods. The proportions of QI value (α -resin) and amounts of β -resin and γ -resin in each pitch powder are compared in Fig. 3. In accordance with the increase in softening point, the QI value of A series pitch increases in association with reduction in amount of β -resin. Pitch B is characterized by minimum QI value and larger amount of β -resin than those of A series pitch powders. Pitch C is characterized by a similar level of QI value to that of A200 and the largest amount of β -resin.

2. 2 Blend compositions of castable refractories

The blending compositions of the castable refractory samples with each pitch powder are shown in Table 2. On the basis of Al_2O_3 -SiC-C blend compositions, each pitch powder was blended with a slightly different added amount. That is, in order to avoid unnecessary influences of the carbon content in the castable refractory on its properties, the added amount of each pitch powder was adjusted so that the fixed carbon in the castable refractory was identical (3%) to one another. With the same amount of water (5.5%) added, all castable refractory samples exhibited a similar level of fluidity.

2. 3 Mechanical strength at elevated temperature

Admixing the same amount of water, each castable refractory mixture was cast into a 40 × 40 × 160 mm mold. Followed by curing at 30 °C for 24 hours

Table 2 Blending compositions of castable refractory samples

Blended pitch powder	A200	A250	A300	B	C
Chemical composition / mass%	Al_2O_3 72 SiC 19 C 3				
Pitch powder content / mass%	4.0	3.9	3.7	3.7	3.9
Water content / mass%	5.5	5.5	5.5	5.5	5.5

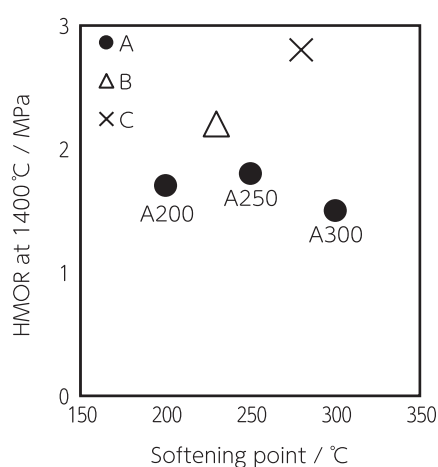


Fig. 4 Relation between softening point of pitch powder and hot modulus of rupture at 1400 °C.

め、ピッチの添加量は配合中の固定炭素量が同一(3%)となるように変化させた。全ての配合において、同一の混練水量で同等の流動性が得られた。

2. 3 熱間強度

各配合を同一水量で混練し、40×40×160mmの形状に流し込み、30℃-24h養生後、110℃-24h乾燥した。その後、コークスブリーズ中で1400℃-3h加熱し、試験サンプルとした。得られた試験サンプルは、1400℃、 N_2 雰囲気下で熱間曲げ強さを測定した。

2. 4 耐食性

試験には110℃-24h乾燥後のサンプルを用いた。侵食試験はアーク加熱回転ドラム法で実施し、侵食剤には高炉スラグ(C/S=1.2)を使用した。試験温度は1600℃、試験時間は5時間とし、侵食剤は1時間毎に入替を行った。試験後、試料の残厚を測定し、耐食性を評価した。

and drying at 110 °C for 24 hours. Dried sample specimens were heated at 1400 °C for 3 hours in a coke breeze. The bending strength (hot modulus of rupture) of each sample specimen was measured at 1400 °C in N_2 atmosphere.

2. 4 Corrosion resistance

The rotary drum corrosion test by arc heating was conducted on sample specimens, which were dried at 110 °C for 24 hours, at 1600 °C for 5 hours with a blast furnace slag of 1.2 basicity (C/S) as corrosive agent, which was completely replaced every hour. After the corrosion test, remaining thickness of each sample specimen was measured to evaluate the corrosion resistance.

3. Results of Experiment

3. 1 Mechanical strength at elevated temperature

The relation between the softening point of blended pitch powder and the hot modulus of rupture of castable refractory is shown in Fig. 4. The relation between the QI value in blended pitch powder and hot modulus of rupture of castable refractory is shown in Fig. 5. No clear correlation between the softening point of the blended pitch powder and hot modulus of rupture of the castable refractory can be observed. Even though a tendency that, in accordance with the increase of the QI value of the blended pitch powder, the hot modulus of rupture of the castable refractory is lowered is observable, castable refractory blended with pitch powder C exhibits much higher hot modulus of rupture than pitch powder A300 with similar level of softening point and pitch powder A200 with similar level of QI value blended. The relation between the amount of β -resin in the blended pitch powder and hot modulus of rupture of castable refractory is shown in Fig. 6. In accordance with increase of amount of β -resin in blended pitch powder, a tendency for the hot modulus of rupture of the castable refractory to increase can be observed with highly clear correlation.

3. 2 Corrosion resistance

The relation between the softening point of the blended pitch powders and corrosion index of castable refractory samples is shown in Fig. 7. The relation between the QI value of the blended pitch powder and corrosion index of castable refractory samples is shown in Fig. 8. In accordance with

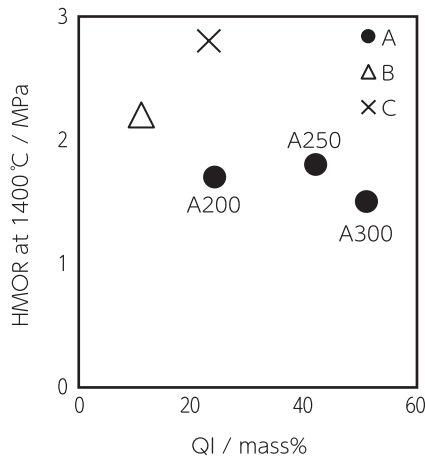


Fig. 5 Relation between QI value in pitch powder and hot modulus of rupture at 1400 °C.

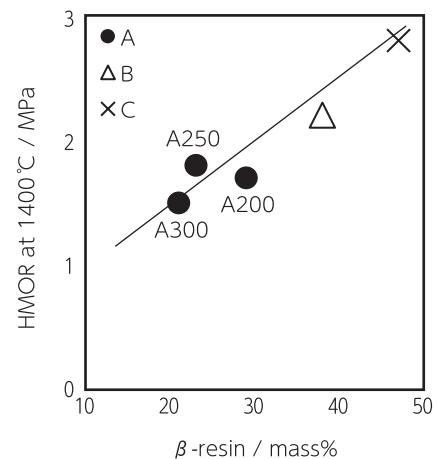


Fig. 6 Relation between amount of β -resin in pitch powder and hot modulus of rupture at 1400 °C.

3. 試験結果

3. 1 熱間強度

Fig.4にピッチの軟化点と熱間曲げ強さの関係、Fig.5にピッチのQI値と熱間曲げ強さの関係を示す。軟化点と熱間曲げ強さには相関が見られなかった。QI値の上昇に伴い熱間曲げ強さは低下する傾向が認められるが、ピッチCは同等の軟化点をもつピッチA300や、同等のQI値をもつピッチA200と比較して熱間曲げ強さが高かった。Fig.6にピッチの β -レジジン量と熱間曲げ強さの関係を示す。 β -レジジン量の増加に伴い熱間曲げ強さは増加する傾向であり、全てのピッチ種において高い相関性が認められた。

3. 2 耐食性

Fig.7にピッチの軟化点と侵食指数の関係、Fig.8にピッチのQI値と侵食指数の関係を示す。軟化点やQI値の上昇に伴い侵食指数は増加する傾向が認められるが、ピッチCは同等の軟化点をもつピッチA300や、同等のQI値をもつピッチA200と比較して侵食指数が低かった。Fig.9にピッチの β -レジジン量と侵食指数の関係を示す。 β -レジジン量の増加に伴い侵食指数が低下する傾向であり、全てのピッチ種において高い相関性が認められた。

4. 考察

ピッチCを使用した材料は熱間強度や耐食性が大幅に向上するという結果が得られた。この要因に関してQI値と β -レジジン量から考察した。Fig.10にQI値と β -レジジン量の違いにより、形成されるカーボンボンドの変化について模式図を示す。鈴木らの報告では、QIは気孔へのピッチ成分の拡

the increase of softening point or QI value of the blended pitch powder, a tendency for the corrosion index of castable refractory samples to increase is observable. However, castable refractory blended with pitch powder C exhibits much smaller corrosion index than pitch powder A300 with similar level of softening point and pitch powder A200 with similar level of QI value is blended. The relation between the amount of β -resin in blended pitch powder and corrosion index of castable refractory sample is shown in Fig. 9. There is a clear correlation that, in accordance with the increase in amount of β -resin in the blended pitch powder, corrosion resistance of castable refractory is improved.

4. Discussions

The experiment results revealed that the hot modulus of rupture and corrosion resistance of the castable refractory blended with pitch powder C were markedly improved. This infers that much powerful carbon bonding is formed in castable refractory body containing the pitch powder C. Focusing on the QI value and amount of β -resin in pitch powder, the differences in carbon bonding formation were examined by referring to the schematic illustration shown in Fig. 10. Suzuki et al. concluded that, since the QI component suppresses diffusion of pitch ingredients into pores in the refractory body, the mechanical strength at elevated temperatures as well as corrosion resistance of the refractory to which pitch powder with low QI value is blended

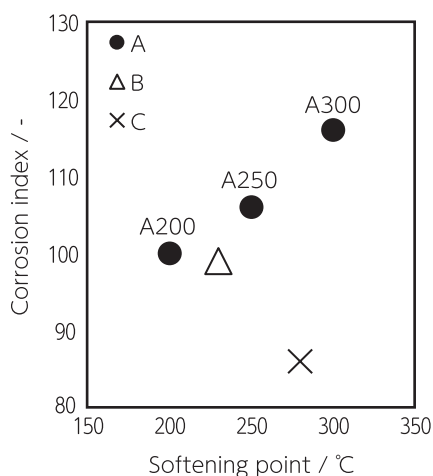


Fig. 7 Relation between softening point of pitch powder and corrosion index.

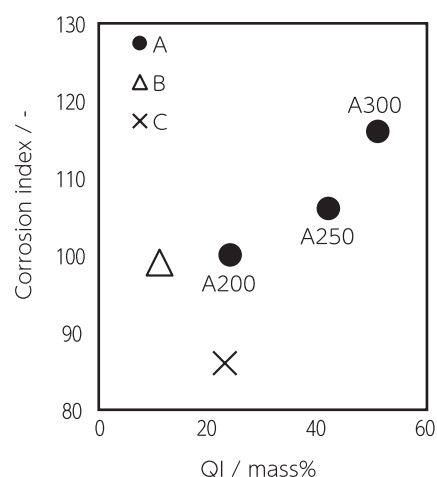


Fig. 8 Relation between QI value in pitch powder and corrosion index.

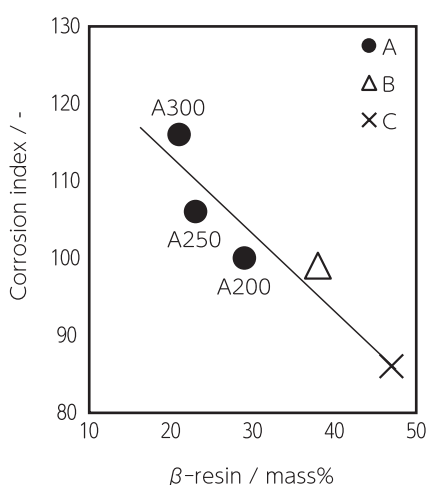


Fig. 9 Relation between amount of β -resin in pitch powder and corrosion index.

are improved³⁾. It is inferred that, when pitch powder with a high QI value is blended, pitch ingredients are not diffused uniformly and thoroughly into pores in refractory body, resulting in quite localized carbon bonding formation. β -resin is one of the major pitch ingredients used for carbon bonding formation. The degree of bonding is regulated by the amount of β -resin to some extent. It is inferred that, since β -resin component in pitch powder C can be diffused thoroughly throughout the refractory body because of the low QI value, a much stronger carbon bonding is formed by an ample amount of β -resin.

It can be concluded from the above discussions that the QI value and amount of β -resin in pitch powder greatly influence the mechanical strength and corrosion resistance of castable refractories, which indicates that, along with the softening point,

QI value	Low	High	Low
Amount of β -resin	Low	Low	High
Schematic illustration of structure around pitch			
Used pitch powder	A200	A250, A300	B, C

Weak carbon bonding
 Strong carbon bonding

Fig. 10 Schematic illustration showing differences in carbon bonding formation by QI value and amount of β -resin in pitch powder.

散を阻害するため、QI値が低い程熱間強度や耐食性が向上したと結論づけられている³⁾。例えばQI値の高いピッチを使用した場合には、材料気孔中へのピッチの拡散が不十分となり、カーボンボンドの形成が局所的になると考えられる。また、 β -レジン⁴⁾はピッチの結合成分であり、 β -レジン量がカーボンボンドの結合力を決定していると推測すると、ピッチCはQI値が低いために材料気孔中へのピッチ成分の拡散が容易であったことに加え、 β -レジン量が多く、他のピッチを使用した場合に比べて強固なカーボンボンドが形成されたと推察される。以上より、QI値と β -レジン量は強度や耐食性に大きく寄与することが示唆され、軟化点と同様にピッチ選定時の重要な指標であると考えられる。今回の試験結果からは、強度や耐食性を考える上で、ピッチのQI値が低く、 β -レジンが多いことが好ましいといえる。

5. まとめ

高炉樋用流し込み材におけるピッチ種の影響について調査を行い、以下の知見を得た。

- ・ピッチの β レジン量と熱間強度や耐食性には相関が見られ、 β レジン量が多いほど熱間強度と耐食性が増加する傾向であった。
- ・ピッチCを使用した材料は、他のピッチ種を使用した場合と比較して強度や耐食性が高くなった。これは、QI値が低いために材料気孔中へのピッチ成分の拡散が容易であったことに加え、 β レジン量が多く、強固なカーボンボンドが形成されたためと考えられる。

these two characteristics of pitch powder, QI value and amount of β -resin, are important guidepost for selecting pitch powder to be blended into castable refractories for the blast furnace trough. In short, pitch powder with low QI value and large amount of β -resin is preferable for blending into castable refractories for the blast furnace trough.

5. Conclusion

The following conclusions were obtained by investigating the influences of the characteristics of pitch powder blended into castable refractory for the blast furnace trough.

- ・ A clear correlation was observed between the amount of β -resin in blended pitch powder and physical properties, such as hot modulus of rupture and corrosion resistance of castable refractories. There was a tendency for the hot modulus of rupture and corrosion resistance of castable refractory to improve in accordance with the increase in the amount of β -resin in the blended pitch powder.
- ・ Castable refractories to which pitch powder C was blended exhibited greatly improved mechanical strength and corrosion resistance. It is inferred that, since pitch ingredients are diffused thoroughly into the refractory body because of the low QI value, much strong carbon bonding is formed throughout the refractory body because of the ample amount of β -resin.

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