

SHINAGAWA TECHNICAL REPORT

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－ Effects of Aluminum Nitride Addition on Changes of
Taphole Mix Properties by Long-time Heating －

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要 旨

窒化珪素鉄を窒化アルミニウムに置換したマッド材の長時間加熱後の特性調査を行った。窒化アルミニウムを多く含むマッド材は、窒化珪素鉄を多く含むマッド材で確認された著しい重量減少、多孔質化が抑制される傾向が確認された。窒化珪素鉄は長時間加熱されることで、窒化珪素に含まれる窒素を放散させる反応が起こる。一方で、窒化アルミニウムは試料外からのCOガスを還元し、マッド材中にカーボンを析出させる反応が生じたことに起因すると推測された。窒化珪素鉄から窒化アルミニウムに置換することは、長い深度を維持し、炉壁保護の役割を向上させる有効な手段であると考えられる。

Abstract

Long heating time induced changes of taphole mix properties in which aluminum nitride was substituted for ferro silicon nitride were investigated. It was affirmed that marked weight loss and change to a loosened porous structure, both of which have been observed in ferro silicon nitride containing taphole mix sample specimens after long heat treatment time, were suppressed in aluminum nitride containing taphole mix sample specimens after long-time heat treatment time. Ferro silicon nitride is decomposed by long heating time accompanied with emission of decomposed nitrogen gas out of the system, which causes structure deterioration of the taphole mix body. It is inferred that aluminum nitride functions as a reducing agent of CO gas coming from outside of the system associated with C precipitation in the taphole mix body, with which slag resistance of taphole mix is secured even after long heating time. It was expected that, by substituting aluminum nitride for ferro silicon nitride, the slag resistance of “mushroom” in blast furnace tap hole would be improved, resulting in sustention of proper “depth” parameter as well as improvement of taphole inner wall protection.

1. 緒言

マッド材は高炉の出鉄孔閉塞材であり、安定した高炉の操業を支えるだけでなく、出鉄孔周辺の炉壁保護の役割も担う。マッド材は炉内に充填された後、出鉄孔周辺に堆積基盤を形成する (Fig.1) ことが知られている¹⁾。炉壁保護の

1. Introduction

In addition to its primary function of stable blast furnace operation, i.e., properly closing taphole through which hot metal produced in blast furnace is discharged, taphole mix plays another important

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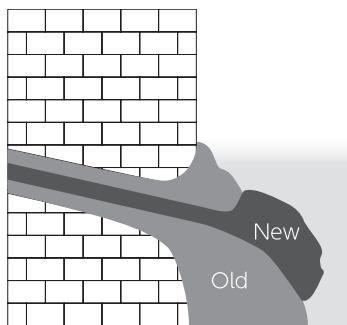


Fig. 1 Schematic illustration of “mushroom” formed with taphole mix in blast furnace taphole .

管理項目として、出鉄孔炉外から炉内方向におけるマッド材が残存する距離である深度が挙げられ、マッド材における重要な評価項目の一つとなっている²⁾。

休風中における高炉出鉄孔のコアボーリングサンプルから、炉内のマッド材はコークスやスラグを含んだ状態であることが報告されている³⁾。また、炉内に堆積されたマッド材は、充填後に炉内であまり時間が経過していない新材、充填後に炉内で長い時間が経過した旧材に大別される⁴⁾。特に旧材では、多量のスラグが侵入しているコアサンプルが得られ、そのコアサンプルを1570℃で再加熱するとスラグが流出し小片化したことから、実炉においても出鉄時の再加熱により、スラグ侵入層を境界として、剥離損傷が生じる可能性が報告されている⁴⁾。また、マトリックス部を酸化物主体で構成したマッド材にスラグを内包し、一軸方向に200kPaの荷重をかけ1500℃で加熱すると、マッド材が崩壊した試験結果が報告されている⁵⁾。これらのことから、上述した剥離損傷が深度低下における大きな原因の一つとなる可能性があり、マッド材には高い耐スラグ性が求められる。また、堆積基盤の多くの部分は旧材で構成されていることが予想されるため、長時間高温に曝されても高い耐スラグ性を維持することが重要である。

高い耐スラグ性を得るため、マッド材では窒化珪素鉄が多量に使用されている⁶⁾。一方で、長時間高温に曝されることで窒化珪素鉄の分解反応が生じ、著しい重量減少を伴い、組織が多孔質化し、耐スラグ性を低下させることが報告されている⁷⁾。このことから、窒化珪素鉄は深度低下の原因の一つとなる可能性があると推測される。本報では、窒化珪素鉄に代わる窒化物として窒化アルミニウムに着目し、長時間加熱されたマッド材の特性に与える影響について調査した。

role of protecting the taphole inner wall. It is acknowledged that, as schematically illustrated in Fig. 1, a so-called “mushroom” is formed inside the blast furnace taphole by periodically being filled in with taphole mix¹⁾. In fact, a “depth” parameter, longitudinal direction distance in taphole where filled-in taphole mix properly remains, is a prominent control item for taphole inner wall protection as well as one of the practical evaluation items of taphole mix²⁾.

It has been reported that, by observation of core-boring samples taken from the blast furnace taphole during cessation of operation, filled-in taphole mix is contaminated with coke and/or slag³⁾. As indicated in Fig. 1, “mushroom” in the blast furnace taphole is roughly divided into “new” material, which has not been in the taphole long, and “old” material, which has been in the taphole for a long period⁴⁾. It has been reported that, when “old” core-boring samples, which contain large amounts of slag, are heated up to 1570℃, the contained slag is remelted. This is associated with sample fragmentation, which indicates of a possibility in practical operation that piled-up taphole mix layers could peel off from the slag contaminated boundary by the reheating of hot metal tapping operation⁴⁾. It has also been reported that, when slag containing taphole mix sample, with a matrix composed mainly of oxide materials, was heated up to 1500℃ under 200 kPa of uniaxial stress, the taphole mix sample collapsed⁵⁾. It is suggested by these reports that the above mentioned peel-off damage is one of the factors lowering the “depth” parameter and sufficiently high slag resistance needs of taphole mix. It is thought that, even with the prospect that the majority of “mushroom” in a blast furnace taphole would be composed of “old” material, slag resistance of taphole mix should be properly maintained even after long exposure to high temperature.

In order to secure high slag resistance, a large amount of ferro silicon nitride is blended into taphole mix⁶⁾. It has been reported that, because of decomposition of ferro silicon nitride by long exposure time to high temperature, the slag resistance of taphole mix is lowered, associated with marked weight loss

2. 試験内容

2.1 供試試料

Table 1に試験配合を示す。試験配合はマッド材で一般的な SiO_2 -(Fe) Si_3N_4 -C質とし、試料Aから試料B, C, Dにかけて、窒化珪素鉄を減量し、窒化アルミニウムへの置換率を0, 14, 29, 100%と変化させた。各配合物を加温した万能ミキサーで約20分間混練し、それぞれのバインダー添加量は押し出し抵抗値の指標であるマーシャル値が同じになるように調整した。混練後、5.0MPaで加圧成形し、コークスブリーズに詰めた状態で、それぞれ加熱処理を行った。長時間加熱された際の特性の変化を検討するため、新材を1500℃-3h加熱と見立て、旧材を1500℃-24h加熱と見立てて各特性を比較した。

2.2 侵食試験

評価方法はアーク加熱を用いた回転ドラム法による侵食試験で行い、侵食剤は高炉スラグを使用し、1時間ごとに入れ替えた。試験温度は1550℃、試験時間は2時間とし、試験後の侵食深さから損耗速度を算出した。また、新材から旧材へと加熱時間の経過による耐スラグ性低下の度合いを、1500℃-3h加熱後試料と1500℃-24h加熱後試料の損耗速度比で数値化して評価した。

耐スラグ性低下指数 = $\frac{1500^\circ\text{C}-24\text{h}\text{加熱後損耗速度}}{1500^\circ\text{C}-3\text{h}\text{加熱後損耗速度}}$

指数が大きい程、長時間加熱による耐食性の低下が大きいことを示す。指数が1以下の場合、長時間加熱後の方が耐スラグ性に優れることを示す。

2.3 物性試験, 化学分析, 粉末X線回折

各供試試料について、重量変化率、見掛気孔率の測定を行った。また、新材から旧材へと加熱時間の経過による重量減少と、多孔質化の度合いを、1500℃-3h加熱後試料と1500℃-24h加熱後試料の重量減少比と見掛気孔率比で

and change to a loosened porous structure⁷⁾. It was consequently inferred that ferro silicon nitride could be one of the possible factors for worsening the “depth” parameter. Putting attention on aluminum nitride, substitutable nitride of ferro silicon nitride, effects of aluminum nitride addition on changes of taphole mix properties, especially, slag resistance, after long time exposure to high temperature are studied in this report.

2. Experiment

2.1 Sample preparation

The raw material blend compositions of the taphole mix samples are summarized in Table 1. Based on generally applied SiO_2 -(Fe) Si_3N_4 -C system taphole mix, four taphole mix samples were prepared by substituting aluminum nitride for the usually added ferro silicon nitride stepwisely by 0 % (sample A), 14 % (sample B), 29 % (sample C) and 100 % (sample D). Specifically, the aluminum nitride addition was increased from 0 % (sample A) to 5 % (sample B), 10 % (sample C) and 35 % (sample D). Each blended mixture was mixed for roughly 20 minutes by planetary mixer. The amount of binder added was adjusted so that each taphole mix sample would exhibit a similar level of Marshal value, an index of the pushing-out resistance of taphole mix. Sample specimens prepared by pressure forming with 5.0 MPa of forming pressure were packed in a coke breeze and heat treated at 1500 °C for 3 hours and for 24 hours. For evaluating differences in taphole mix property changes caused by exposure to high

Table 1 Composition of samples

Composition / mass%	Sample name	A	B	C	D
	Pyrophyllite	40			
	Clay	10			
	Carbonaceous material	15			
	Ferro silicon nitride	35	30	25	-
	Aluminum nitride	-	5	10	35
Substitution rate from ferro silicon nitride to aluminum nitride / %		0	14	29	100
Coal tar / mass%		21.6	21.4	21.1	20.0

数値化して評価した。

重量減少指数 = 1500°C -24h加熱後重量減少率 / 1500°C -3h加熱後重量減少率

多孔質化指数 = 1500°C -24h加熱後見掛気孔率 / 1500°C -3h加熱後見掛気孔率

それぞれの指数が大きい程、長時間加熱により、重量減少、多孔質化が進行することを示す。

また、試料の一部を粉砕し、化学分析、粉末X線回折の評価を行った。

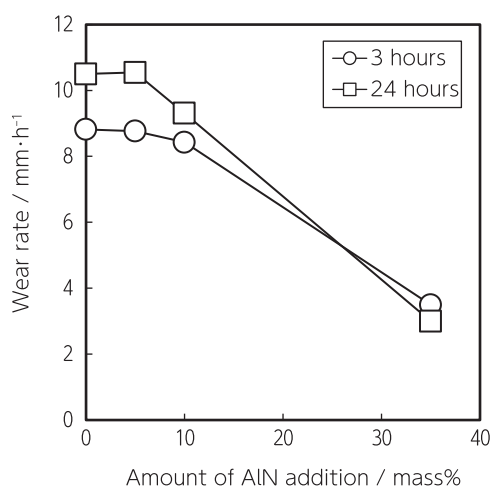


Fig. 2 Change in experimentally evaluated wear rate as a function of the amount of aluminum nitride after heating at 1500°C for 3 and 24 hours.

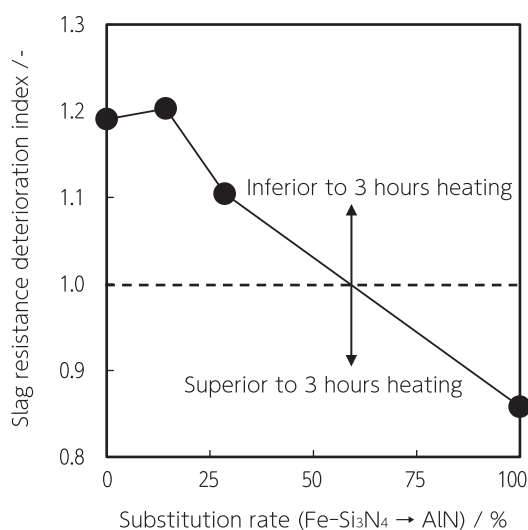


Fig. 3 Influence of substitution rate of aluminum nitride for ferro silicon nitride on slag resistance deterioration index.

temperature time, different heat treatment times were applied. That is, for simulating “new” and “old” taphole mix material, 3 hours and 24 hours of heat treatment time were respectively applied. Changes in properties of heat-treated taphole mix sample specimens were mutually compared. It is noted that taphole mix sample specimen heat-treated at 1500°C for 3 hours and for 24 hours is hereinafter referred to as “3 hour (or short time) heat-treated” and “24 hours (or long time) heat-treated” sample specimen, respectively, without explicit notation of heat treatment temperature.

2. 2 Corrosion test

Corrosion behaviors of heat-treated taphole mix sample specimens were evaluated in a rotating drum type corrosion test with electric arc heating at 1550°C for 2 hours with blast furnace slag as corrosive agent, which was exchanged every one hour. After the corrosion test, the wear rate was calculated by the corrosion depth of the sample specimen. To study the degree of slag resistance change caused by heat treatment time, namely, the difference of slag resistance between “new” and “old” taphole mix material, the ratio of wear rate between the 24 hour heat-treated sample specimen and 3 hour heat-treated sample specimen was used as the “slag resistance deterioration index”. That is, “slag resistance deterioration index” is defined with (wear rate of 24 hour heat-treated sample specimen) / (wear rate of 3 hour heat-treated sample specimen).

A larger value of “slag resistance deterioration index” consequently means more marked deterioration of slag resistance by exposure to high temperature. Lower than 1 (one) of “slag resistance deterioration index” signifies that slag resistance of long time heat-treated sample specimen is superior to that of short time heat-treated sample specimen.

2. 3 Measurement of physical and chemical properties and XRD analysis

Weight change of the sample specimens as well as apparent porosity of each heat-treated sample specimen were measured. For evaluating the difference of weight change and apparent porosity between “new” and “old” taphole mix material,

3. 実験結果

3.1 侵食試験

Fig.2に1500℃-3, 24h加熱後における各試料の損耗速度の結果を示す。いずれの加熱時間に関わらず、窒化アルミニウムへの置換により損耗速度が低下する傾向が確認された。Fig.3に、各試料の耐スラグ性低下指数を示す。窒化アルミニウムへ置換することで、長時間加熱による耐食性の低下を抑制する傾向が確認された。また、全量置換では長時間加熱後の方が耐スラグ性に優れる結果が得られた。

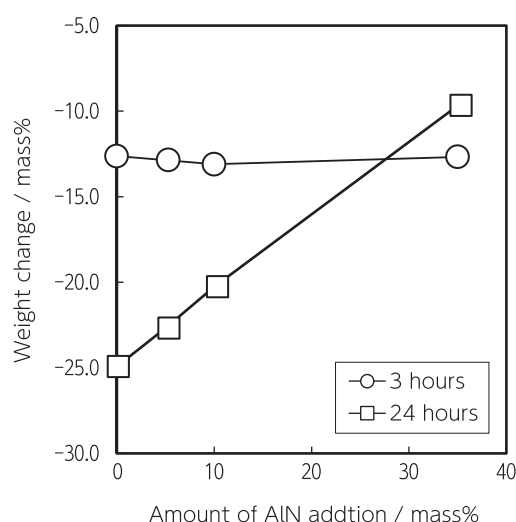


Fig. 4 Variation in weight change as a function of the amount of aluminum nitride after heating at 1500 °C for 3 and 24 hours.

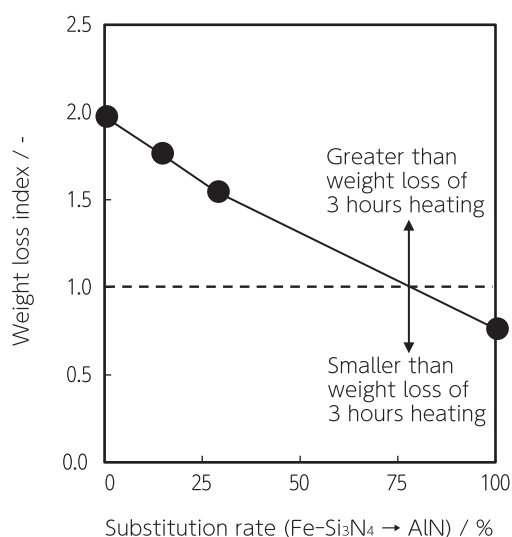


Fig. 5 Influence of substitution rate of aluminum nitride for ferro silicon nitride on weight loss index.

“weight loss index” and “porosity increase index” were defined as follows with using measured physical property values.

Weight loss index = (weight change of 24 hour heat-treated sample specimen) / (weight change of 3 hour heat-treated sample specimen)

Porosity increase index = (apparent porosity of 24 hour heat-treated sample specimen) / (apparent porosity of 3 hour heat-treated sample specimen)

Therefore, a larger value of weight loss index and porosity increase index signifies higher susceptibility of weight reduction and structure loosening associated with porosity increase to long time heating, respectively.

Chemical composition analysis and powder X-ray diffraction (XRD) analysis were conducted with crushed pieces of sample specimens.

3. Results of Experiment

3.1 Corrosion test

The change in the experimentally evaluated wear rate as a function of the amount of aluminum nitride after heating at 1500 °C for 3 and 24 hours is shown in Fig. 2. Regardless of heat treatment time, the wear rate was lowered in association with an increase in the amount of aluminum nitride. The influence of the substitution rate of aluminum nitride for ferro silicon nitride on the slag resistance deterioration index is shown in Fig. 3. A tendency for, in accordance with increase of substitution rate of ferro silicon nitride with aluminum nitride, the lowering of slag resistance by long exposure time to high temperature to be suppressed is clearly observable. It is noteworthy that sample D, in which whole ferro silicon nitride is substituted for aluminum nitride, exhibits smaller than 1 (one) of slag resistance deterioration index, indicating of superior slag resistance of long heat-treatment time sample specimen.

3.2 Physical properties

Variation in weight change as a function of the amount of aluminum nitride and change in apparent porosity as a function of the amount of aluminum nitride is shown in Fig.4 and Fig.6, respectively.

3. 2 物性

1500℃-3, 24h加熱後における各試料の重量変化率をFig.4に, 1500℃-24h加熱後の重量変化指数Fig.5に示す。1500℃-3, 24h加熱後における各試料の見掛け孔率をFig.6に, 1500℃-24h加熱後の多孔質化指数をFig.7に示す。Fig.4より, 窒化アルミニウムへの置換により1500℃-24h加熱の重量減少が小さくなる傾向が確認された。Fig.5より, 窒化アルミニウムへの置換により, 1500℃-3h加熱と1500℃-24h加熱の重量減少差が小さくなり, 全量

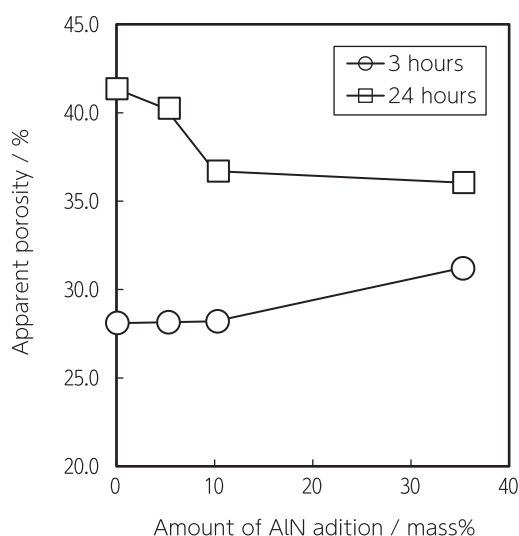


Fig. 6 Change in apparent porosity as a function of the amount of aluminum nitride after heating at 1500℃ for 3 and 24 hours.

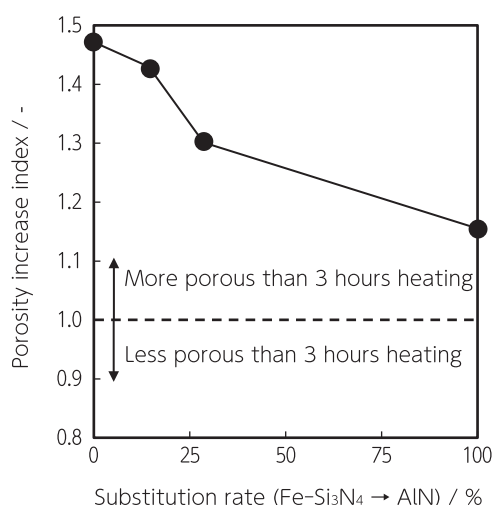


Fig. 7 Influence of substitution rate of aluminum nitride for ferro silicon nitride on porosity increase index .

Based on these measurements, weight loss index and porosity increase index of four taphole samples were calculated and plotted as a function of the substitution rate of aluminum nitride for ferro silicon nitride in Fig. 5 and Fig. 7, respectively. It is observable in Fig. 4 that, in accordance with the increase in the amount of aluminum nitride, the weight loss of long heat-treatment time sample specimen was markedly lessened. A clear tendency for, in accordance with increase of substitution rate of ferro silicon nitride with aluminum nitride, the weight loss index to be gradually lowered is observed in Fig. 5. Sample D in which aluminum nitride is completely substituted for ferro silicon nitride exhibits smaller than 1 (one) of weight loss index, which means that weight loss induced by 24 hour heat treatment is smaller than that by 3 hour heat treatment. As per Fig. 6, different tendencies in the change of apparent porosity is observable between 3 hour and 24 hour heat-treated sample specimens. That is, in accordance with the increase of the amount of aluminum nitride, the apparent porosity of the 3 hour heat-treated sample specimen slightly increased, but the apparent porosity of the 24 hour heat-treated sample specimen was contrarily lowered only slightly. Consequently, as per Fig. 7, the porosity increase index is lowered in association with increase of substitution rate of aluminum nitride for ferro silicon nitride, which means that change to loosened and porous structure is suppressed by increase of aluminum nitride addition.

3. 3 Chemical compositions

The influence of amount of aluminum nitride addition on total nitrogen content and free carbon content of heat-treated sample specimen is shown in Fig. 8 and Fig. 9, respectively. Regardless of the added amount of aluminum nitride, the total nitrogen content of the 24 hour heat-treated sample specimen is lower than that of 3 hour heat-treated sample specimen. The free carbon content of sample A, B and C, in which the added amount of ferro silicon nitride is greater than that of aluminum nitride, has been lowered by long heat treatment time. However, sample D, in which aluminum nitride

置換すると1500℃-24h加熱後の重量減少は1500℃-3h加熱後より小さくなることが認められた。Fig.6より、窒化アルミニウムへの置換により、1500℃-3h加熱後の見掛け気孔率は高くなり、1500℃-24h加熱後の見掛け気孔率は低下する傾向が確認された。Fig.7より、窒化アルミニウムへの置換により、1500℃-24h加熱による多孔質化が抑制される傾向が確認された。

3. 3 化学分析

Fig.8, 9に1500℃-3, 24h加熱後における各試料のTotal nitrogen, Free Cの変化を示す。Total nitrogenに

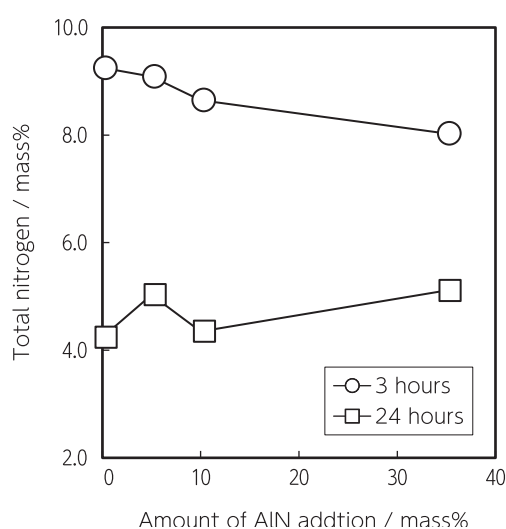


Fig. 8 Influence of amount of aluminum nitride addition on total nitrogen content of heat-treated sample specimen.

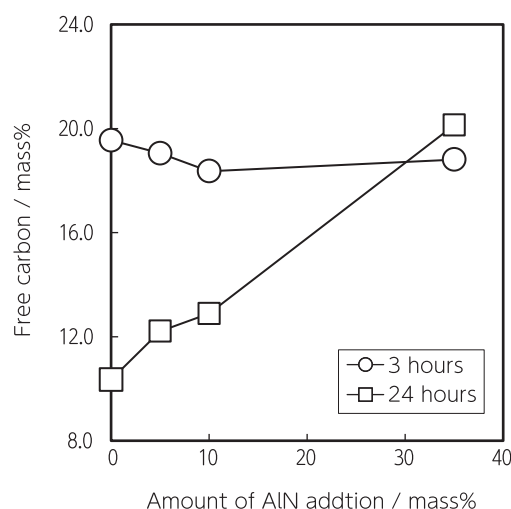


Fig. 9 Influence of amount of aluminum nitride addition on free carbon content of heat-treated sample specimen.

was completely substituted for ferro silicon nitride, exhibited higher free carbon content after 24 hour heat treatment than after 3 hour heat treatment, meaning an increase of free carbon content by long heating time.

3. 4 Powder X-ray diffraction analysis

X-ray diffraction patterns of sample A (no substitution of aluminum nitride for ferro silicon nitride) and sample D (complete substitution of aluminum nitride for ferro silicon nitride) are shown in Fig. 10 and Fig. 11, respectively. The sharp diffraction peak of β - Si_3N_4 , which is observed in diffraction patterns of 3 hour heat-treated sample A, is diminished after heat treatment at 1500℃ for 24 hours. Instead, diffraction peaks of β -SiC and $\text{Si}_2\text{N}_2\text{O}$ can be identified in diffraction pattern of 24 hour heat-treated sample A. The sharp diffraction peak of AlN, which is observed in diffraction patterns of 3 hour heat-treated sample D, was almost eliminated after heat treatment at 1500℃ for 24 hours. Instead, a diffraction peak of SiAlON is detectable in the X-ray diffraction pattern of 24 hour heat-treated sample D. In addition, diffraction peak of corundum, which is identifiable in X-ray diffraction patterns of 3 hour heat-treated sample D, intensified after heat treatment at 1500℃ for 24 hours.

4. Discussions

As indicated with Fig. 5, 7 and 8-10 and pointed out in precedent reports, marked weight loss associated with change to loosened porous structure is induced in the taphole mix body by thermal decomposition of ferro silicon nitride, especially under long heating time conditions^{7,8)}. Chemical reactions of ferro silicon nitride have been variously reported^{9,10)}. Based on experiment results in this study, it is inferred that chemical reactions of ferro silicon nitride proceed as per the schematically illustrated procedures shown in Fig. 12. It is clarified with Fig. 8-10 that both total nitrogen and free carbon content of ferro silicon nitride containing taphole mix is lowered by long heat treatment time in association with formation of SiC and $\text{Si}_2\text{N}_2\text{O}$. Since ferro silicon nitride is a chemical compound composed of Fe and Si_3N_4 ,

については、いずれの試料も1500℃-24h加熱後は1500℃-3h加熱後より減少する傾向が確認された。一方で、Free Cについては、窒化珪素鉄を多く含む試料A, B, Cは、1500℃-3h加熱後に比べて1500℃-24h加熱後は著しく減少したが、試料Dは、1500℃-3h加熱後に比べて1500℃-24h加熱後の方が増加することが確認された。

3. 4 粉末X線回折

Fig.10, 11に1500℃-3, 24hで加熱した、試料A, Dの粉末X線回折パターンを示す。窒化珪素鉄のみの試料Aは、1500℃-3h加熱後では明瞭な β - Si_3N_4 のピークが確認されたが、1500℃-24h加熱後ではピークが小さくなり、

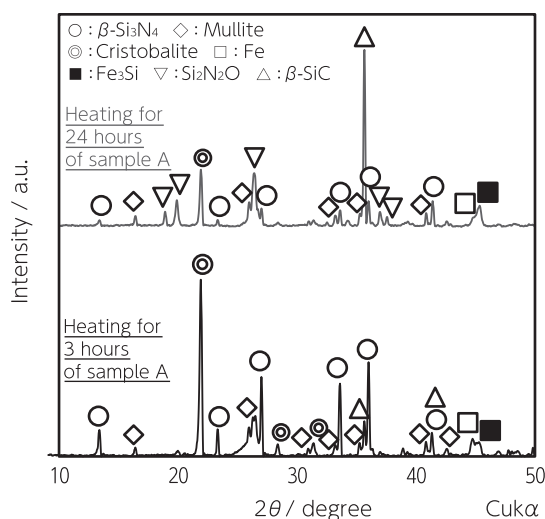


Fig. 10 X-ray diffraction patterns of sample A heat-treated at 1500℃ for 3 and 24 hours.

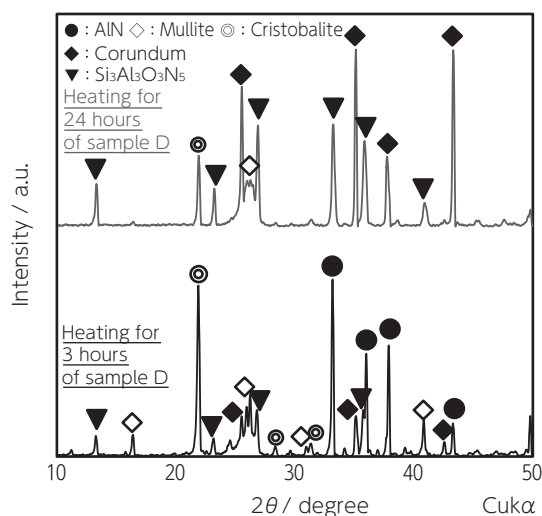


Fig. 11 X-ray diffraction patterns of sample D heat-treated at 1500℃ for 3 and 24 hours.

components of C, Fe and Si_3N_4 coexist with oxide materials in ferro silicon nitride containing taphole mix. It is inferred that Fe-C liquid phase is formed by the supply of CO gas generated by the reaction between Fe and carbon raw material or coke breeze as well as by direct supply from carbon raw material. Since it has been reported that, when SiC is formed from ferro silicon nitride, mass transfer of the Si component in Si_3N_4 is accompanied by some manner¹⁰⁾, it is inferred that the Si component is transferred into Fe-C liquid phase and forms Fe-C-Si ternary compound system liquid phase. It is also inferred that, since C and Si components are continuously supplied after the formation of Fe-C-Si liquid phase, these components are oversaturated and SiC is formed, accompanied by emission of N_2 gas out of Si_3N_4 . Formation of $\text{Si}_2\text{N}_2\text{O}$ can be explained with the following inference. It is known that, with Si_3N_4 and SiO_2 as starting materials, $\text{Si}_2\text{N}_2\text{O}$ is generally synthesized by liquid phase reaction with the aid of a small amount of added sintering agent such as Al_2O_3 ¹¹⁾. Referring to the report that glassy Si-(Al)-O-N system network was observed near hot surface of corrosion test taphole mix specimen¹²⁾, it is inferred that $\text{Si}_2\text{N}_2\text{O}$ is formed by liquid phase reaction between Si_3N_4 and oxide materials in this study.

Because of the lowering of C and Si contents in Fe-C-Si liquid phase induced by SiC formation, C and Si components are continuously supplied, resulting in oversaturation and another SiC formation associated with N_2 gas emission. It is inferred that marked weight loss and change to loosened and porous structure of long heat-treatment time taphole mix sample specimen are induced by repetition of such reaction process. It is also inferred that change to loosened and porous structure causes deterioration of slag resistance after heat treatment at 1500℃ for 24 hours. Prospecting that “mushroom” in blast furnace taphole is formed majorly with “old” material with deteriorated slag resistance, such a situation is thought to be one of the causes for reduction of the “depth” parameter in practical blast furnace operation.

While, as is obvious with Fig.5 and Fig.7, in

新たに β -SiC, $\text{Si}_2\text{N}_2\text{O}$ のピークが確認された。一方で、窒化アルミニウムのみを試料Dは、 1500°C -3h加熱後では明瞭なAlNのピークが確認されたが、 1500°C -24h加熱後ではピークがほぼ消滅し、新たにSiAlONのピークが確認された。また、 1500°C -3h加熱後にコランダム（ Al_2O_3 ）のピークが確認され、 1500°C -24h加熱後はピークが大きくなることが確認された。

4. 考察

Fig.5, 7, 8-10やこれまでの報告から、長時間加熱の条件下において、窒化珪素鉄の分解反応により、マッド材の著しい重量減少、多孔質化が起こることが分かっている^{7),8)}。窒化珪素鉄の化学反応には、様々な報告がなされているが^{9),10)}、今回の実験ではFig.12に示すような反応が生じたと推測する。Fig.8-10より、窒化珪素鉄を含むマッド材では長時間加熱により、Total nitrogen, Free Cが低下し、SiC, $\text{Si}_2\text{N}_2\text{O}$ を生成する反応が確認された。窒化珪素鉄は Si_3N_4 とFeが共存する複合原料であり、窒化珪素鉄を含むマッド材組織中では、C, Fe, Si_3N_4 、酸化物が共存し

accordance with increase of substitution rate of aluminum nitride for ferro silicon nitride, both weight loss index and porosity increase index is lowered. In other words, combination of weight loss and change to loosened and porous structure, which was significantly observed in ferro silicon nitride containing taphole mix samples, is suppressed in aluminum nitride containing taphole mix samples with a tendency that, in accordance with increase of aluminum nitride addition, degree of such suppression becomes intensive. Especially, weight loss of 24 hour heat-treated sample D specimen, in which aluminum nitride was completely substituted for ferro silicon nitride, is smaller than that of 3 hour heat-treated specimen. These experiment results strongly indicate that different kind of reactions take place in aluminum nitride containing taphole mix samples. Under coexistence of C, stable phases of Al in mixed N_2 and CO gas atmosphere are Al_2O_3 , AlN, Al_4C_3 , C¹³⁾. According to JANAF thermodynamic database¹⁴⁾, these four phases coexist in equilibrium at 1800K under the condition of $\log P_{\text{N}_2} = -5.537$ and $\log P_{\text{CO}} = -2.374$. Taking into account experiment condition in this study, that taphole sample specimens were heat treated in a coke breeze, $\log P_{\text{CO}}$ is thought to be around -0.46 (P_{CO} is around 0.35 atm). It is therefore inferred that the following reaction takes place in the experiment.



In the reaction, CO gas coming from outside the specimen is reduced by AlN and C is precipitated in association with N_2 gas emission to outside of system and formation of corundom. Such reaction is verified by the experiment results that, as shown in Fig.8 and Fig.9, 24 hour heat-treated taphole mix sample specimen exhibits lower total nitrogen content and higher free carbon content than the 3 hour heat-treated sample specimens. Validity of such inference is also verified by, as exhibited in Fig.11, detection of diffraction peak of corundum in powder X-ray diffraction analysis on sample D. It is inferred that, since source of precipitated C is supplied as CO from outside the system, weight increase of the sample specimen is accompanied

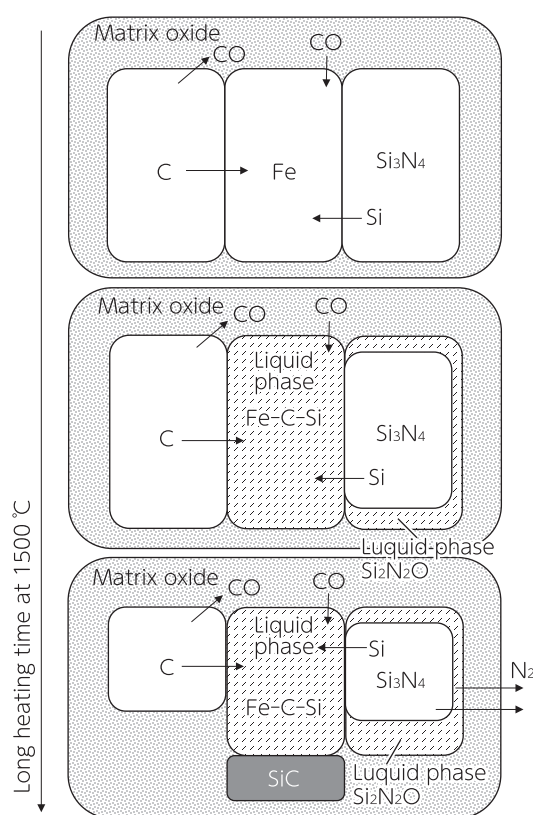


Fig. 12 Schematic image of silicon carbide decomposition and silicon carbide formation procedure in ferro silicon nitride containing taphole mix.

ている。Feに接触するカーボン原料やコークスブリーズから発生するCOガス、接触するカーボン原料から直接Cが供給されることで、Fe-Cの液相が生成すると考えられる。窒化珪素鉄がSiC生成を起こす場合、 Si_3N_4 中のSiは何らかの形態で物質移動することが報告されていることから¹⁰⁾、本実験においても、Fe-C液相に移動し、Fe-C-Siの3元系の液相が生成したと考えられる。Fe-C-Si液相の生成後もC、Siが供給され続けることで過飽和となり、SiCが生成し、同時に Si_3N_4 から N_2 が放出されたと考えられる。 $\text{Si}_2\text{N}_2\text{O}$ の生成については以下のように考察する。一般的に $\text{Si}_2\text{N}_2\text{O}$ の合成は Si_3N_4 と SiO_2 を出発原料とし、 Al_2O_3 等の焼結助剤を少量添加することで、液相を形成して反応させることが知られている¹¹⁾。マッド材においても、侵食試験後の稼働面近傍にSi-(Al)-O-N系のガラス状のネットワーク組織が観察されていることから¹²⁾、本実験においても Si_3N_4 と酸化物の液相反応により生じたものと考えられる。

SiC生成によりFe-C-Si液相のC、Si濃度が低下するため、C、Siが供給され、過飽和となり、SiCを生成、 N_2 ガスを放出するという工程が繰り返されることで、 1500°C -24h加熱後の著しい重量減少、多孔質化が確認されたと考えられる。また、多孔質化により、 1500°C -24h加熱後の耐スラグ性が低下したと考えられ、実炉においては耐スラグ性の低い旧材として堆積基盤を形成するため、深度を低下させる原因の一つとなることが推測される。

Fig.5, 7より、窒化アルミニウムを含有するマッド材では窒化珪素鉄を含有するマッド材に見られた、長時間加熱後の著しい重量減少は確認されず、多孔質化も抑制されていた。特に、 1500°C -24h加熱後の重量減少は 1500°C -3h加熱後の重量減少より小さいことから、窒化アルミニウムは窒化珪素鉄と異なる化学反応が生じたと考えられる。炭素が共存する場合、 N_2 ガスとCOガスが混在する雰囲気下におけるAlの安定相は、 Al_2O_3 、AlN、 Al_4C_3 、Cの4種である¹³⁾。この4種はJANAFの熱力学データから¹⁴⁾、 1800K の場合について、 $\log P_{\text{N}_2}=-5.537$ 、 $\log P_{\text{CO}}=-2.374$ の場合に平衡に共存する。今回の実験は、コークスブリーズ中における還元雰囲気であり、 $\log P_{\text{CO}}=-0.46$ (0.35 atm)程度と考えられるため、今回の実験では以下の反応が生じたと推測される。



この反応ではAlNは試料外からのCOガスを還元して、カーボンを析出させ、 N_2 を試料外に放出し、コランダムを生成する。これは、Fig.8, 9において、Total nitrogenは 1500°C -3h加熱後より 1500°C -24h加熱後の方が少ないこと、一方で、Free Cは 1500°C -3h加熱後より 1500°C -

by the reaction. The experiment results shown in Fig.4 and Fig.5, of the weight loss of 24 hour heat-treated sample D being smaller than that of 3 hour heat-treated sample D supports the validity of such inference. In addition, the experiment results shown in Fig.4 and Fig.5 show that, in comparison with 3 hour heat-treated sample specimens, the degree of weight loss of aluminum nitride containing taphole sample specimens (sample B, C and D) heat-treated for 24 hours was lessened. This indicates that the reaction is promoted by long heating time. As for formation of SiAlON, it is inferred that, similar to $\text{Si}_2\text{N}_2\text{O}$ formation in ferro silicon nitride containing taphole mix, SiAlON is formed by liquid phase reaction between AlN and oxide materials such as SiO_2 .

Regarding a similar kind of reaction, it was reported that, when heating metallic aluminum at 1500°C in a mixed N_2 and CO gas atmosphere, aluminum nitride and C were detected as reaction products after 1 hour heating and Al_2O_3 and carbon were detected after 10 hours heating¹⁵⁾. It is speculated in the report that, due to the lowering of partial pressure of N_2 gas by the reaction between metallic aluminum and CO gas, metallic aluminum is firstly altered to aluminum nitride, followed by the above mentioned alumina formation reaction associated with C precipitation¹⁵⁾.

It is prospected that, since aluminum nitride functions as a reducing agent of CO gas coming from outside of the system, reduced C is precipitated so as to fill pores generated by decomposition of aluminum nitride. It is inferred that change to loosened and porous structure induced by long heating time is suppressed by such C precipitation in aluminum nitride containing taphole mix sample specimens. It is also inferred that, because of precipitation of C which is characterized by low wettability to slag, slag resistance of long heat-treatment time aluminum nitride containing taphole mix sample specimen is superior to that of short heat-treatment time sample specimen.

It is expected that, with substitution of aluminum nitride for ferro silicon nitride, slag resistance of "old" material in "mushroom" is properly secured with

-24h加熱後の方が多いことや、Fig.11において、コランダムのパークが確認されたこと等に共通している。さらに、この反応は重量増加が生じる反応であり、Fig.4, 5において、1500℃-24h加熱後の重量減少は1500℃-3h加熱後の重量減少より小さいことにも共通している。また、それぞれ1500℃-24h加熱後に1500℃-3h加熱後より上記の減少が強まったことから、加熱時間が長くなるに従って、反応がより進行したと推測される。SiAlONの生成については、窒化珪素鉄を含有するマッド材における $\text{Si}_2\text{N}_2\text{O}$ 生成過程と同様で、 AlN と SiO_2 等の酸化物が液相を介して生成したと推測する。

前述の反応と近い現象として、金属アルミニウムを N_2 ガスと CO ガスが混在する雰囲気下で1500℃-1h加熱すると窒化アルミニウムとカーボンが検出され、1500℃-10h加熱では Al_2O_3 とカーボンが検出されたことが報告されている¹⁵⁾。この報告では、金属アルミニウムと CO ガスとの反応によって N_2 ガス分圧が上昇したことで窒化アルミニウムに変化し、その後は前述した反応に移行し、アルミナの生成、カーボンの析出が生じたと考察されている¹⁵⁾。

このように、マッド材中の窒化アルミニウムは試料外からの CO ガスの還元剤として働くことで、窒化アルミニウムの分解によって生じた気孔を封じるようにカーボンが析出し、長時間加熱による多孔質化が抑制されたと考えられる。また、長時間加熱後の多孔質化を抑制しただけでなく、スラグに濡れにくいカーボンをマッド材中に新たに析出させたため、1500℃-24h加熱後は1500℃-3h加熱後の耐スラグ性を上回ったと推測される。

窒化珪素鉄から窒化アルミニウムへの置換は、実炉において耐スラグ性の高い旧材として堆積基盤を形成し、スラグ侵食による剥離損傷を抑制する効果を向上させると考えられる。それにより、安定して長い深度を維持し、炉壁保護の効果も向上することが期待される。

5. まとめ

窒化珪素鉄に代わる窒化物として窒化アルミニウムに着目し、長時間加熱されたマッド材の特性に与える影響について検討し、以下の知見が得られた。

- ・ 窒化珪素鉄を多く含むマッド材は、1500℃-3h加熱後に比べて1500℃-24h加熱後の耐スラグ性が低下した。1500℃-24h加熱後において、著しい重量減少、多孔質化が確認されたことから、組織脆化が起因していると考えられた。また、1500℃-24h加熱後ではTotal nitrogenの減少が確認され、窒化珪素鉄の分解反応が組織脆化の原因であると推定された。

less peel-off damage caused by slag corrosion. It is expected that such improvement effects would be fulfilled as sustainment of stable “depth” parameter and as better performance in taphole inner wall protection.

5. Conclusion

Putting attention on aluminum nitride as a substitutable nitride for ferro silicon nitride, effects of aluminum nitride addition to taphole mix on changes of its properties after long heating time were studied and the following conclusions were obtained.

- ・ The slag resistance of ferro silicon nitride containing taphole mix sample specimen heat-treated at 1500℃ for 24 hours was worse than that of the sample specimen heat-treated at 1500℃ for 3 hours. Marked weight loss and change to loosened porous structure, which were observed in ferro silicon nitride containing taphole mix sample specimen heat-treated at 1500℃ for 24 hours, strongly indicate deterioration of taphole mix body. Reduction of the total nitrogen content, which was more prominent in the 24 hour heat-treated taphole mix sample specimens indicates that structure deterioration is caused by thermal decomposition of ferro silicon nitride.
- ・ The slag resistance of aluminum nitride containing taphole mix sample specimen heat-treated at 1500℃ for 24 hours exceeded that of the sample specimen heat-treated at 1500℃ for 3 hours. Marked weight loss, which was observed in ferro silicon nitride containing taphole mix sample specimens heat-treated at 1500℃ for 24 hours, was eased in association with smaller change to loosened porous structure. Experiment result that free carbon content of aluminum nitride containing taphole mix sample specimen heat-treated at 1500℃ for 24 hours is higher than that of sample specimen heat-treated at 1500℃ for 3 hours indicates that aluminum nitride functions as reducing agent of CO gas coming from outside of system. These experiment results inferred that, since C is precipitated so as to fill pores generated by decomposition of aluminum nitride, deterioration

・窒化アルミニウムを多く含むマッド材は、1500℃-3h加熱に比べて1500℃-24h加熱後の耐スラグ性が向上した。窒化珪素鉄を多く含むマッド材で見られた1500℃-24h加熱後の著しい重量減少は確認されず、多孔質化も抑制されていた。1500℃-24h加熱後では1500℃-3h加熱後と比べてカーボン量が増加しており、試料外からのCOガスの還元剤として働いたことが示唆された。これらのことから、窒化アルミニウムの分解により生じる気孔を封じるようにカーボンが析出することで、1500℃-24h加熱後の組織脆化を抑制したと推測される。また、カーボン量が増加したことにより、1500℃-24h加熱後の耐スラグ性が1500℃-3h加熱後より高くなったと考えられる。

長時間加熱後の組織脆化を抑制する技術を確立した。窒化珪素鉄から窒化アルミニウムへの置換は、長い深度を維持し、炉壁保護の役割を向上させる有効な手段であると考えられる。

of taphole mix sample body is suppressed. It is also inferred that increase of free carbon content in the aluminum nitride containing taphole mix sample specimen by heat treatment at 1500℃ for 24 hours creates better slag resistance than that of the sample specimen heat-treated at 1500℃ for 3 hours.

By substituting aluminum nitride for ferro silicon nitride, structure deterioration of the taphole mix body caused by long heating time was effectively suppressed. It can be concluded that substitution of aluminum nitride for ferro silicon nitride is quite an effective measure for enforcing important roles of taphole mix.

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