Introduction of Refractory Repair Technology

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Abstract

Mist injection shot technology (MIS) and thermite welding technology are developed as new refractory repair technology. MIS is used for blast furnace troughs, degassing vessels and steel ladle repair. Ceramic welding is used for coke oven repair. 1) MIS is designed for improvement of gunning workability and service life by new gunning equipment. 2) Ceramic welding is developed for the enhancement of security. Details of these technologies are introduced in this paper.

1. Mist Injection Shot (MIS) Method

1.1 Outlines

The methods of refractory repair by gunning, or spraying, are roughly divided into two types: dry and wet gunning, each of which has advantages and disadvantages. Figure 1 compares the dry and the wet gunning methods and the newly developed MIS.

By the dry gunning, the refractory material in powder is pneumatically pumped from the material tank through a hose to the gunning nozzle, and then mixed with water there. The equipment is simple to operate, but the water addition mechanism is such that it is difficult to delicately control the water mixing ratio, and due to the high water content of the mixture, the gunned body of the gunned refractory on the repaired surface tends to have many pores, which lowers their durability (see Fig. 1 a). The wet gunning method, on the other hand, is capable of forming a high-density refractory gunned body with low moisture contents, but the pre-mixing and pumping of the slurry require much labor for equipment cleaning after use (see Fig. 1 b). 1–3)

The MIS method presented herein is capable of forming a refractory gunned body of substantially the same quality as those by the wet gunning with the same ease of operation as the dry gunning (see Fig. 1 c).

1.2 Characteristics of MIS method

1.2.1 MIS equipment

Different from the dry and wet gunning methods, the MIS method consists of efficiently adding high-pressure water in mist, or in fine particles, to the refractory powder at two stages during the pneumatic pumping. This water addition method offers remarkably higher kneading efficiency than by conventional methods and enables gunning of low-moisture slurry.

The MIS equipment is composed of a main unit comprising a material powder feeder and controllers for air and water, hoses for the material, air and water, and mist injection nozzles provided at two positions of the material feed line (the primary and secondary mist nozzles in Fig. 1 c).

Figure 2 shows photographs of the mist nozzles. It is possible for the gunning operator to flexibly control the moisture content of the slurry by turning the water injection valve of the secondary nozzle according to the operation condition.

Fig. 1 Comparison of refractory spraying methods
1.2.2 Characteristics of fine water mist

The water mist injection nozzles of the MIS method are twin-fluid nozzles of air and pressurized water to turn water into mist of fine particles. Figure 3 compares the size distribution and the average size of the water particles by the MIS method with the same of conventional dry gunning. Presented here are the analysis results of the size of water particles under the air supply condition for the pneumatic material transfer measured using a phase Doppler interferometer made by TSI Inc. The measured particle size range was 0.5 \( \mu \text{m} \) to 1.0 mm.

The size distribution of the water particles of the MIS injection nozzle is concentrated on the lower side, and the average size is 11 \( \mu \text{m} \), roughly one-third that of the nozzle for the conventional dry gunning.

Figure 4 compares the water spray of the injection nozzle of the MIS method with that of the common dry gunning: whereas water is sprayed in coarse and fine particles in a wide angle from the latter, it is ejected in fine uniform mist from the former.

1.2.3 Effects of fine water particles

Table 1 schematically illustrates the situations of water injection into a material powder flow in the nozzles for the MIS method and that for the conventional dry gunning. The structure of the injection nozzle of the conventional method is such that the water injected in a powder flow is distributed unevenly and its penetration into the powder flow stream is limited. Consequently, the water addition amount required for desired slurry fluidity tends to be large. In preparing the material powder, in addition, it is necessary to take measures such as adding an excessive amount of binder so that the slurry moisture stays within the range adequate for gunning operation in consideration of the water amount fluctuating locally and periodically.

By the MIS method, in contrast, water is injected in particles smaller than those of the material powder, the water particles cut into the material flow stream from all directions through powder grains, high-speed fine water particles easily reach the center of the stream, the water permeates in the entire material powder instantaneously, and the powder quickly turns into homogeneous slurry. Accordingly, the water addition is limited to the least necessary for forming a slurry adequate for gunning.

1.3 Refractory material

1.3.1 Characteristics of refractory material for MIS

Figure 5 shows the properties of the gunned body of different refractory materials formed by gunning, and Fig. 6 the temperature range of the object surface suitable for different gunning methods. Generally speaking, there is a certain relationship between the water content of the slurry and the structure of its gunned body, and accordingly, low water content of the gunning slurry has been targeted to obtain a gunned body of high density.

Dry gunning is viable in a wide temperature range from cold to hot by suitably selecting the material, but at high temperature, the porosity of the gunned body tends to be high as water addition increases. Cement bond type materials are mainly used for wet gunning; they are suitable for low water contents to obtain a high-density gunned body, but this method is applied mainly to cold repair.

The material for the MIS method is designed such that, in combination with the equipment, the high-density gunned body strongly bonded to the repaired surface is formed at hot repair offering long durability due to the low water content of the sprayed slurry.

It is characterized, more specifically, by (1) blending of the material for low-moisture spraying based on the concept of low-moisture slurry for mold casting, (2) selection of a high-reactivity binder for good bonding of low-moisture slurry to the object surface, and (3) mitigating the effects of vapor generation at hot spraying to form...
a highly dehydrated gunned body having good bonding to the repaired surface. As a result, the gunned body of the MIS method exhibits strong bonding and high durability under the conditions of hot spraying.

1.3.2 Formation of high-density gunned body

Figure 7 shows the characteristics of the sprayed gunned body obtained by the MIS and the conventional dry gunning methods. Presented here are the porosities of the gunned body of the Al₂O₃-MgO material widely used for repairing the lining of steel ladles, and the water volume of the sprayed slurry. The combination of the MIS equipment and the material makes it possible to greatly lower the slurry moisture, and as a result, the density of the gunned body increases. The tests show that when the MIS equipment is used for spraying the material for conventional dry gunning, the material cannot be sprayed at as low a water content as that of the MIS powder, and that when the equipment for dry gunning is used for the MIS material, the water injection and kneading capacity are insufficient, and workability and adhesion of the gunned body to the object surface are poor.

1.3.3 Adhesion and bonding of gunned body to object surface

The major cause of the damage to the refractory gunned body formed by hot repair is detachment. Accordingly, to secure good adhesion and a wide area of contact between the gunned body and the object surface, it is essential for the sprayed slurry to adhere well to the surface at the instant of contact. The slurry can be made to adhere to the object surface by accelerating its change into a gel, and the adhesion of the gunned body is strengthened by controlling the water content of the slurry as low as possible, and accelerating the dehydration of the gunned body to quickly disperse the vapor of the slurry moisture from the contact surface. In consideration of the above, the MIS powder contains a highly reactive binder, and its composition is designed to secure good permeability at high temperature.

Figure 8 compares the dehydration performance of the same gunned body as those of Fig. 7 formed by the MIS and conventional hot gunning; here each of the materials was kneaded to a water content suitable for spraying by respective methods, cast in a metal mold, charged promptly into an oven maintained at 800°C, and the dehydration was continuously measured based on the weight decrease in the oven. The MIS gunned body, in spite of its high density, began to dehydrate immediately after the start of heating, which suggests that the adverse effects of the vapor generation on the bonding interface are mitigated.

Figure 9 shows the appearance of a gunned body formed by the MIS method at 900°C, and a sectional photomicrograph of its bonding interface. Another sectional photomicrograph of a gunned body formed by conventional dry gunning at the same temperature is given for comparison purposes. The MIS gunned body is well bonded to the object surface with few gaps at the interface.

1.3.4 Quality of MIS material

Table 2 shows the chemical composition and physical properties of the materials and gunned body of the MIS method for different applications. The gunned body of any of these materials exhibits high density and strength. The two Al₂O₃-MgO materials are for the hot repair of steel ladles and RH degassers; the one for RH degassers is used also for the automatic spray repair of the inner walls of the snorkels, and in consideration of the short spray distance, the blending ratio of the aggregates and the binder and the grain size distribution of the aggregates are changed partially from those for ladles.

The Al₂O₃-SiC material has actually been used for the hot repair of the main troughs of blast furnaces.

1.4 Durability

Figures 10 and 11 show examples of the durability of the MIS gunned body formed in hot repair of steel ladles and BF main troughs, respectively. The MIS gunned body, when applied to steel ladles, withstood 16 charges on a common wall surface, 5 charges at
the slag line, and 3 to 5 charges at the bottom near the discharge port, demonstrating 1.6 times the durability, sometimes over twice, of those by conventional dry gunning. With BF main troughs, MIS has demonstrated durability roughly twice that by conventional dry gunning, greatly contributing to extension of the service life of the trough.

**Fig. 8** Dehydration of refractory gunned body by MIS and dry gunning (at 800°C)

**Fig. 9** Good adhesion of MIS material (at 900°C)

**Fig. 10** Durability of MIS gunned body on steel ladles

**Fig. 11** Durability of MIS gunned body on BF main trough (metal line on the upstream side)

**Table 2** Chemical composition and physical properties of MIS gunned body

<table>
<thead>
<tr>
<th>Composition</th>
<th>Al₂O₃-MgO</th>
<th>Al₂O₃-MgO</th>
<th>Al₂O₃-SiC</th>
</tr>
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<tbody>
<tr>
<td>Chemical analysis</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(mass%)</td>
<td>Al₂O₃</td>
<td>73</td>
<td>73</td>
</tr>
<tr>
<td>SiC</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MgO</td>
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<td>15</td>
<td></td>
</tr>
<tr>
<td>SiO₂</td>
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<td>6</td>
<td></td>
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<tr>
<td>Grain size distribution</td>
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<td>Top particle size (%)</td>
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<td>3</td>
</tr>
<tr>
<td>+1 mm (%)</td>
<td>33</td>
<td>20</td>
<td>35</td>
</tr>
<tr>
<td>−0.075 mm (%)</td>
<td>28</td>
<td>27</td>
<td>27</td>
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<tr>
<td>Apparent porosity (%)</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>(°C × 3h)</td>
<td>22.4 (1500)</td>
<td>25.2 (1500)</td>
<td>28.5 (1450)</td>
</tr>
<tr>
<td>Bulk density (°C × 3h)</td>
<td>2.74 (1500)</td>
<td>2.60 (1500)</td>
<td>2.53 (1450)</td>
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<td>Cross-bending strength (MPa)</td>
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<tr>
<td>(°C × 3h)</td>
<td>11.8 (1500)</td>
<td>11.5 (1500)</td>
<td>5.4 (1450)</td>
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<tr>
<td>Permanent linear expansion</td>
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<tr>
<td>(°C × 3h)</td>
<td>+0.15 (1500)</td>
<td>+0.90 (1500)</td>
<td>+0.56 (1450)</td>
</tr>
<tr>
<td>Application</td>
<td>Steel ladles</td>
<td>RH degassers</td>
<td>BF main troughs</td>
</tr>
</tbody>
</table>
2. Thermite Welding with Enhanced Safety Measures

2.1 Outlines

The term “thermite welding” comes from the thermite reaction of metallic silicon with oxygen expressed by Equation (1) to generate a large amount of heat. The process is characterized by the ease of operation compared with flame gunning and the absence of adverse effects on the refractory to be repaired caused by the slurry water of dry gunning, and as such, it has been effectively used for the hot repair of coke ovens.

\[
\text{Si} + \text{O}_2 = \text{SiO}_2 + \text{heat}
\]  

(1)

On the other hand, it involves high-speed pneumatic transfer of powder material containing metallic Si with oxygen gas and the Si + O₂ combustion at the refractory surface to be repaired, and consequently, there is always the danger of backfire and unexpected ignition. The present section explains the measures that we took to decrease the possibility of danger to the very minimum.

2.2 Process of thermite welding

Coke ovens are repaired in heat using unshaped refractories by the methods of dry gunning, flame gunning, and thermite welding; the most suitable method is selected in consideration of factors such as the surrounding conditions of the oven, the portion to be repaired, and the type of damage.

Figure 12 shows the principle of thermite welding, and Fig. 13 the configuration of the equipment. The process consists of pneumatic transfer of a mixture of refractory and metallic Si in powder using oxygen gas, spraying them through a nozzle, and having the Si oxidize (thermite reaction) at the surface to be repaired so that the refractory material is quickly melted by the reaction heat and forms a gunned body there. The durability of the gunned body obtained is superior to that of dry gunning, which involves material agglomeration and hardening through reactions with water, but inferior to that of flame gunning, whereby the material is melted for a comparatively long time in the combustion flame of propane and oxygen and solidified on the object surface.

For the thermite welding process to start it is necessary to receive heat from the object surface, but when it is not hot enough, the work can be started using a gas burner or some other ignitor. In this case, however, the sprayed material is not melted sufficiently, and the adhesion and durability of the gunned body tend to be poor. In addition, when the distance from the nozzle to the object surface is too short, the sprayed material rebounds, and the danger of backfire due to excessive heating of the nozzle increases, and when the distance is too large, on the other hand, the combustion becomes insufficient and the adhesion and durability tend to be poor: it is important to keep the distance at 50 to 100 mm. The operation of thermite welding is made easier with a simplified and light-weight equipment system, while the durability and bonding strength of the gunned body and work safety generally depends on the condition of the surface to be repaired and the operators’ skill.

2.3 Safety measures

2.3.1 Main problems, danger, and countermeasures

The main problems of thermite welding are (1) backfires and (2) unexpected ignition. Either of them may lead to a serious accident, but the safety of the process can be secured by taking adequate countermeasures.

(1) A backfire occurs when the combustion speed of the material exceeds the oxygen flow rate in the nozzle; it is often triggered by rebound material grain entering the nozzle or an increase in the material combustion rate due to the temperature rise of the nozzle during work inside a hot oven. Moments before a backfire, sparks are seen to flash out from the nozzle in most cases, and it can be prevented from occurring by closing the oxygen flow at the sight of them and before the fire enters the material feed line. The countermeasures against backfires consist of (i) suppression of its occurrence, (ii) procedures at the sight of the warning sign, and (iii) prevention of secondary accidents.

(2) Unexpected ignition is the combustion of the refractory material in the feed line triggered by a spark or an electrostatic discharge during its transfer at high speeds; it occurs without any previous warning signs. Its countermeasures consist of (i) suppression of its occurrence, and (ii) prevention of secondary accidents.

In the case of either a backfire or unexpected ignition, the material burns violently in the oxygen atmosphere in the feed line, and unless adequate measures are quickly taken, the material, the hoses, and other combustible parts of the equipment will be lost, and moreover, burning material may be ejected from the broken hose together with the oxygen, leading to an extremely dangerous situation. It is therefore essential to avoid its occurrence and take quick measures to prevent secondary accidents.

2.3.2 Countermeasures against backfire

(1) Preventive measures

A backfire is caused by nozzle clogging by rebounding refractory material or the like, oxygen leakage due to wear and breakage of the material feed line, and reduction of the oxygen flow rate that may result from various anomalies. When a burning lump of the
material rebounds and enters the nozzle, it is also highly likely to cause a backfire. Overheating of the nozzle is another possible cause.

The countermeasure against backfires on the equipment side is to use a small-diameter nozzle. When the nozzle diameter is small, the oxygen flow speed increases to reduce the likelihood of a backfire. To prevent a backfire from occurring, the equipment measures alone are insufficient: it is essential to take operational measures such as inspecting before use as to whether there is clogging of the nozzle, wear of the material feed line possibly leading to breakage, bending of the hose, reduction of the oxygen pressure in the feed line, etc. Changing an overheated nozzle with a cooler one is another operational measure, but this depends on the judgment of the operator.

(2) Quick action before and at the occurrence of a backfire

Figure 14 shows an overview of the thermite welding apparatus. There are no measures to prevent a backfire completely, but in most cases visible signs of one appear a little before its occurrence, and the apparatus is equipped with a foot pedal to stop the oxygen flow; it is connected to the apparatus with a hose and it is possible if needed to stop the operation from a safe position. Although the operator’s decision and intervention are required, it is possible to prevent a backfire by adequately actuating the pedal, and even after a backfire has occurred, it is possible to prevent secondary accidents by quick action.

2.3.3 Countermeasures against unexpected ignition

(1) Preventive measures

Unexpected ignition of the spray material is caused by the sparks of the spray material’s collision with the feed line and electrostatic discharge due to causes such as friction. Since the necessary elements of ignition are a heat source (an ignitor or fire), oxygen, and combustible material, the countermeasures against ignition consist of eliminating or minimizing any one of them. Although it is practically impossible to eliminate any one of oxygen, combustible material, and fire completely, it is possible to control them.

On the equipment side, the occurrence of fire is minimized by removing protrusions on the inner surface of the material feed line as far as possible and avoiding the use of a material that is prone to cause sparks at collision (common carbon steel) for the feed line. Burrs on the inner surface are removed at the manufacturing stage, and the lance and the nozzle, which are used inside a hot oven, are made of stainless steel, which has the same heat resistance and strength as those of carbon steel but emits fewer sparks at collision. In addition, the apparatus has a grounding cable to be connected to a backstay or some oven structural member made of metal to prevent electrostatic discharge.

Other measures have been taken in terms of the material composition so as to avoid ignition even when all the three factors of combustion are given. The prerequisites for work safety are to maintain the apparatus free from oxygen leakage, keep the oxygen pressure as prescribed, and operate the apparatus in prescribed conditions under the prescribed setting of operating parameters. The chemical composition of the spray material is designed such that its injection amount from the nozzle is kept below the lower limit concentration of explosion with respect to the oxygen flow rate; by this it is possible to maintain a condition where combustion does not advance even when the three necessary factors for combustion are temporarily given. To raise the lower limit concentration of explosion, or to hinder the progress of combustion, it is necessary to lower the Si content in the refractory material, but this means less heat generated by its oxidation leading to poorer durability of the refractory gunned body. This problem has been solved by adding MgO, which reacts with molten SiO₂ as in Equations (2) and (3) to generate heat. Figure 15 schematically illustrates the exothermic reactions between MgO and SiO₂.

\[
\begin{align*}
\text{Si} + \text{O}_2 \rightarrow \text{SiO}_2 \\
\text{SiO}_2 + \text{MgO} \rightarrow \text{MgSiO}_3 \\
\text{Si} + \text{O}_2 + \text{MgO} \rightarrow \text{MgSiO}_3
\end{align*}
\]

The increase in heat generation by the MgO addition greatly improved the melting of the sprayed material compared with the former material designed to be melted only by the reaction heat of Si. Table 3 compares the properties of the welding gunned body of the materials with and without the MgO addition. Conventionally, the weld gunned body of thermite welding was porous and often contained many unmelted grains, but since the MgO addition, their bulk density has been markedly increased, and as a result, their bonding strength and crushing strength improved significantly.

(2) Quick action at the occurrence of unexpected ignition

At present, there are no measures to completely prevent unexpected material ignition, but the apparatus is provided with devices to suppress secondary disasters: one is a blow-up lid of the material tank acting as a pressure release mechanism, and the other is a limit switch to automatically stop the oxygen blowing actuated by the blow-up of the lid. The foot pedal mentioned earlier is another
emergency stop device to be actuated by the operator as a stand-by in the unlikely event of the above automatic stop mechanism failing to work.

3. Summary

3.1 MIS method

The characteristics of the developed MIS method are summarized as follows:

(1) A spray gunned body of the same bulk density as that of the gunned body by wet gunning can be obtained with an equipment system as easy to operate as that for dry gunning.

(2) The gunning work is simple as material kneading before the work and hose cleaning after it are not required.

3.2 Safety measures for thermite welding

(1) Thermite welding is capable of forming a highly durable refractory gunned body by simple operation. Since water is not used, no damage is inflicted on the refractory surface to be repaired. As such, the process is indispensable for hot repair of coke oven refractories.

(2) Although it is impossible to perfectly prevent backfires and unexpected ignition of the spraying material by measures related to the apparatus and the material, and operators’ intervention is always required, every conceivable measure to prevent accidents has been incorporated in the apparatus, and the method has been successfully used for oven repair.

(3) A next generation apparatus is expected to be lighter in weight and easier to operate, offering the same safety.

References

6) Honda et al.: Taikabutsu. 65 (9), 439–442 (2013)

| Table 3 | Chemical composition and properties of gunning gunned body |
|-----------------|-----------------|-----------------|
| **MgO addition** | **Conventional** |
| SiO₂ | 72 | 81 |
| MgO | 10 | – |
| Bulk density | 2.21 | 1.3 |
| Apparent porosity (%) | 8.7 | 41.3 |
| Hot adhesive strength (MPa)* | 3.1 | 0.3 |
| Cold crushing strength (MPa)* | 124 | 40 |

* Surface temperature of silica brick 900°C.