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# Magnesia-Carbon Refractories for Converters

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**Abstract**

***Magnesia-carbon (MgO-C) refractories are composed of magnesia clinker, flake graphite, antioxidants, and resin. Due to the components, they exhibit high corrosion resistance, spalling resistance, and slag infiltration resistance. MgO-C refractories have been partially applied to converters since the late 1970s and are now used in all converter parts. By changing the components according to the damage type of each part of the converter, the refractory greatly contributes to improving the life of the converter and reducing the cost of refractory. Furthermore, higher durability has been achieved through the development of new evaluation methods, reduction of graphite, and suppression of the MgO-C reaction.***

## 1. Introduction

Magnesia-carbon (MgO-C) bricks were developed for use on the hot spots of electric arc furnaces and began to be applied to converters in the late 1970s. Since they were found to have higher durability than dolomite-carbon bricks that were mainly used for converters then,[1] they have significantly increased in use applications and quantities as converter refractories. Today, MgO-C bricks are widely applied as steelmaking refractories, not only for converters but also for vacuum degassers and ladles, among other equipment.

MgO-C bricks are composed of magnesia clinker, flake graphite, antioxidants, resin components, etc., and have high resistance to corrosion, spalling, and slag penetration thanks to the characteristics of their constituents. Furthermore, their strength and physical properties, corrosion resistance, and spalling resistance can be significantly changed by changing the particle size composition of magnesia clinker and the addition contents of flake graphite and antioxidants. In actual operation, the blend composition of MgO-C brick raw materials is finely tuned to suit the wear pattern of specific converter lining areas. The zoned lining method is employed to use different refractories in different converter lining zones. As a result, the converter life is extended and the converter refractory cost is reduced.

## 2. Raw Material Composition

Typical constituent raw materials of MgO-C bricks are outlined below.

### 2.1 Magnesia clinker

Sintered magnesia and electrofused magnesia are mainly used for MgO-C bricks. **Table 1** shows typical quality examples of sintered magnesia and electrofused magnesia.[2] The purity, crystal grain size, crystal grain boundary flux $CaO/SiO_2$ ratio, and other properties of magnesia clinker affect the corrosion resistance of MgO-C bricks.[3] It is necessary to select appropriate aggregate types to suit specific converter lining areas.

### 2.2 Graphite

Natural flake graphite is commonly used for MgO-C bricks. Graphite in MgO-C bricks is not easily wetted by slag and suppresses slag infiltration. It also inhibits spalling with its high thermal conductivity and low coefficient of thermal expansion. In addition, CaO

**Table 1 Typical quality examples of magnesia clinker**

| | | Sea-water | | Natural | |
|---|---|---|---|---|---|
| | | Electro-fused | Sintered | Electro-fused | Sintered |
| Chemical compositions (%) | $SiO_2$ | 0.2 | 0.22 | 1.29 | 1.96 |
| | $Al_2O_3$ | 0.06 | 0.06 | 0.12 | 0.9 |
| | $Fe_2O_3$ | 0.11 | 0.04 | 0.75 | 0.67 |
| | CaO | 0.57 | 0.51 | 1.19 | 0.98 |
| | MgO | 99.07 | 99.13 | 96.55 | 95.46 |
| | $B_2O_3$ | 0.02 | 0.04 | – | – |
| Apparent porosity (%) | | 2.6 | 1.5 | 1.1 | 8.0 |
| Bulk specific gravity | | 3.46 | 3.4 | 3.54 | 3.20 |
| Radius of periclase ($\mu$m) | | 200< | 20–40 | 50< | 20–60 |

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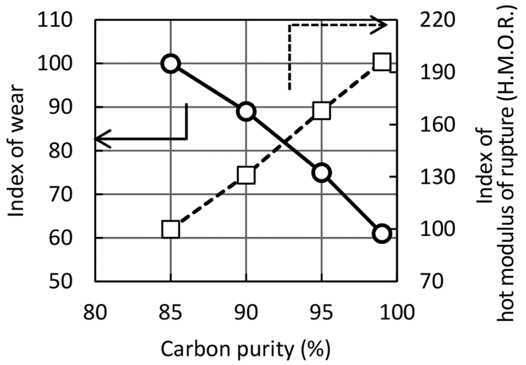


**Fig. 1 Relationship of carbon purity and wear, hot modulus of rupture**

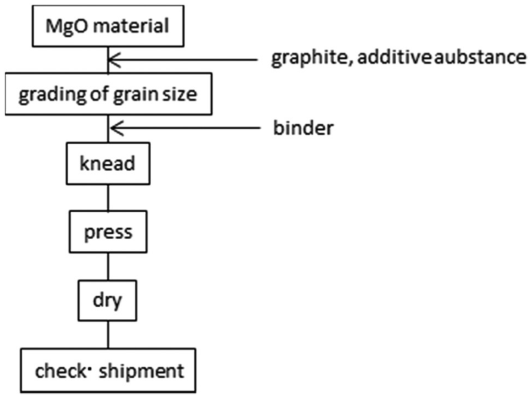


**Fig. 2 Manufacturing flow of bricks**

**Table 2 Reaction of oxidation resistant material**

| Oxidation resistant material | Reactions |
|---|---|
| Al | $2Al(l) + 3CO(g) = Al_2O_3(s) + 3C(s)$ |
| Si | $Si(s) + C(s) = SiC(s)$ |
| B4C | $B_4C(s) + 6CO(g) = 2B_2O_3(l) + 7C(s)$ |

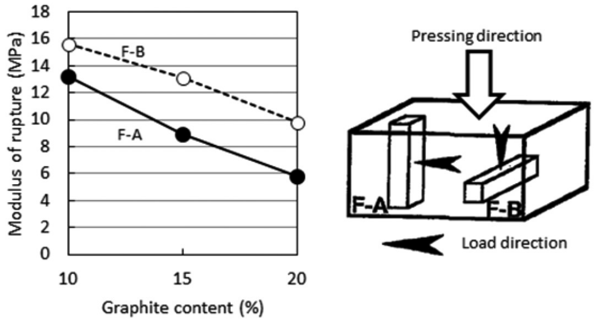


**Fig. 3 Anisotropy of MgO-C bricks modulus of rupture**

and $SiO_2$ contained in the ash of graphite migrate to the boundaries between graphite and magnesia clinker at high temperature and form low-melting point compounds. The low-melting point compounds are considered to form liquid phases, reducing the hot modulus of rupture of MgO-C bricks and facilitating the dissolution of the magnesia clinker into the slag.[4, 5] High-purity graphite is often used as a component of MgO-C bricks for the converter lining areas where high corrosion resistance is required (**Fig. 1**).

**2.3 Resins**

Phenolic resin is generally used as binder for magnesia clinker, graphite, and other raw materials in MgO-C bricks.[6] The phenolic resin

- Has high affinity for and is kneaded well with graphite and magnesia clinker.
- Is high in fixed carbon and forms strong carbon bonds.
- Is less harmful to environmental health than tar pitch.

Phenolic resin comes in two types: the thermosetting resol type and thermoplastic novolac type. The type to be used is determined by considering the manufacturing process, manufacturing equipment, and other conditions.

**2.4 Other additives**

Carbon components contained in MgO-C bricks are oxidized by oxygen and carbon dioxide in the atmosphere or by iron oxide in the slag. Antioxidants such as metals are added mainly to suppress this oxidation. Typical antioxidants and their reactions are summarized in **Table 2**.[7]

## 3. Manufacturing Process

**Figure 2** shows a typical MgO-C brick manufacturing flow sheet. The respective steps are described below.

First, the raw materials are graded into coarse, medium, and fine sizes and are classified as necessary. Next, they are mixed and kneaded with a binder in predetermined blend proportions by particle size. The kneaded mixture is press formed into bricks.

Uniaxial forming with an oil press or a friction press is generally adopted as the pressing method. The magnesia clinker and graphite in MgO-C bricks exhibit orientability depending on the forming direction of the press. The strength and thermal conductivity of MgO-C bricks exhibit anisotropy[8] (**Fig. 3**). It is therefore important to consider the forming direction of bricks when laying the bricks. A cold isostatic press (CIP) with small anisotropy is also used for the manufacture of large refractory products such as bottom blowing tuyere bricks and tap hole bricks.

Formed bricks are dried to remove moisture and other volatile components, processed and coated as required, visually inspected for cracks, chips, and other defects, and shipped after removing defective bricks.

## 4. Wear Mechanisms of MgO-C Bricks

The basic wear mechanisms of MgO-C bricks are roughly classified into the following five.

**4.1 Corrosion**

The dissolution and elution phenomena of magnesia clinker by slag can be divided into the following two:

- Dissolution and elution of the magnesia clinker by intrusion of the $SiO_2$ and CaO components into the periclase grain boundaries in the magnesia clinker
- Dissolution of the periclase by diffusion of the FeO component into periclase crystals (melting point reduction by formation of MgO-FeO complete solid solution)

The above phenomena proceed at the same time. In any case, the dissolution and elution phenomena of the magnesia clinker into the slag greatly affect the wear mechanism of MgO-C bricks.[9] This is supported by the fact that high-purity raw materials and electrofused magnesia with few grain boundaries are applied to badly damaged areas, that the MgO content of the slag during blowing is intentionally increased, and that the wear rate of bricks is reduced by coating with the slag whose MgO content is adjusted.

### 4.2 Oxidation

The carbon contained in the MgO-C bricks plays the role of suppressing the penetration of slag components into the bricks, but it also has the drawback of being oxidized. The carbon oxidation phenomena can be divided into the following three types:

- Liquid phase oxidation
- Gas phase oxidation
- Oxidation of carbon by MgO (MgO-C reaction)

Liquid-phase oxidation is mainly caused by iron oxides in the slag. The iron oxide concentration in the slag has a great influence on the wear rate of MgO-C bricks.[10] As expressed by the reaction formula of $FeO(s)+C(s)\rightarrow Fe(s)+CO(g)$, this phenomenon gasifies the carbon comprising the matrix of the brick and induces the structural embrittlement of the brick. **Figure 4** shows an example of liquid phase oxidation. Highly brilliant Fe precipitates are confirmed in the void layer below the working surface or immediately below the void layer.

Gas phase oxidation is the phenomenon by which the carbon in the brick matrix burns. It is caused by oxygen and carbon dioxide in the atmosphere. In general converters, gas-phase oxidation is likely to become a problem in the converter cone that is not adequately protected with slag and is easily exposed to air. A common remedy is the preliminary addition of active metal powder or similar material to the brick mixture as described in Section 2. The MgO-C reaction is a phenomenon likened to the wear mechanism of MgO-C bricks and will be described in detail in the next section.

### 4.3 MgO-C reaction

The oxidation reaction of carbon in MgO (MgO-C reaction) is given by

$$MgO(s) + C(s) \rightarrow Mg(g) + CO(g)$$

Whether this reaction proceeds to the right depends on the temperature, Mg partial pressure, and CO partial pressure. The reaction is controlled by the dissipation rate of Mg(g) and CO(g) from the working surface of the lining. **Figure 5** shows an Ellingham diagram at various magnesia and CO partial pressures.[11] In the equilibrium state where each partial pressure is 1 atm, the above reaction starts at 1 850°C. If either or both of Mg(g) and CO(g) fall below 1 atm, the reaction proceeds from the left to the right. In a refractory that can be regarded as an open system, formed Mg(g) diffuses and the Mg partial pressure in the refractory decreases considerably. As a result, the above reaction occurs at a significantly low temperature and causes the structural embrittlement of the refractory.[11]

### 4.4 Spalling

Spalling damage is classified into thermal spalling and mechanical spalling. **Figure 6** shows the relationship between the graphite content and spalling resistance.[12] Generally, the higher the content of graphite with high thermal conductivity, the smaller the temperature gradient in the thickness direction of the refractory lining becomes. That is, the thermal expansion difference in the refractory lining decreases and the spalling resistance improves. Converters are generally lined with MgO-C bricks with a graphite content of 15 to 20 mass%. Given the large effect of equipment availability, MgO-C bricks with higher graphite contents are often used in intermittently operating electric arc furnaces, for example.

Mechanical spalling is caused by the thermal stress produced when the refractory lining thermally expands under restraint conditions. Mechanical spalling is likely to occur in the converter lining after a relatively few heats. Generally, the converter lining continuously peels off in the circumferential direction. If mechanical spalling occurs, the stress concentrations in the converter lining are mitigated by measures such as providing expansion allowance joints, changing brick allocations, and adjusting the number of joints.

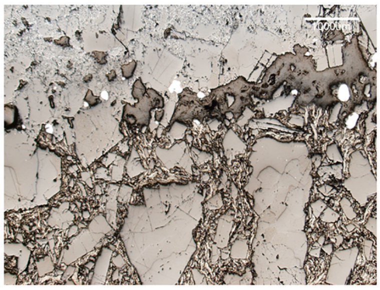

**Fig. 4 Working surface structure of MgO-C brick with liquid phase oxidation**

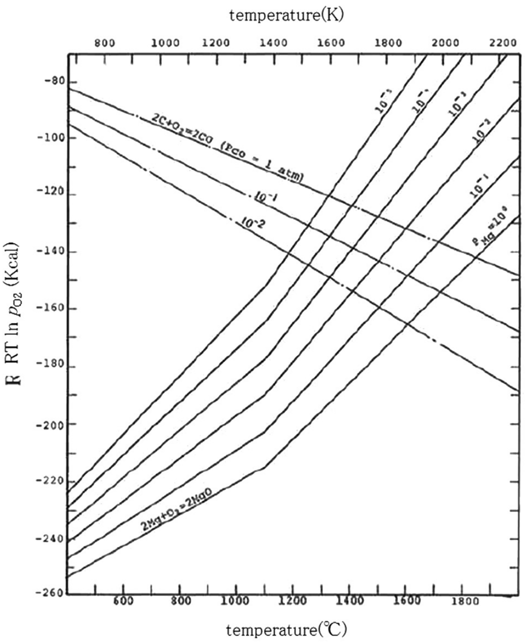


**Fig. 5 Ellingham diagram**

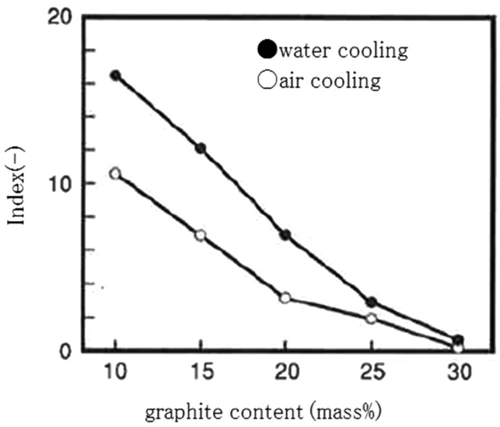


**Fig. 6 Graphite content and spalling resistance**

### 4.5 Abrasion

Among the damage of MgO-C bricks in converters, abrasion damage by the molten steel is likely to occur especially in the bottom and tap hole areas. These lining areas are characteristic in that the slag and molten steel coexist and flow together, that the slag coating layer is difficult to form, and that the molten steel flow causes the dislodgement and outflow of graphite and magnesia clinker pieces. **Figure 7** shows the relationship between the wear by the molten steel and the hot modulus of rupture. The wear by the molten steel decreases as the hot modulus of rupture increases.[13] The hot modulus of rupture can be effectively improved by structural densification or metal addition.

## 5. Characteristics of MgO-C Bricks and Their Application to Specific Converter Lining Areas

In the design of the converter refractory lining, the respective lining areas differ in the damage mechanism, frequency, and amount. Zoned lining is generally adopted for changing the thickness and quality of MgO-C bricks in different lining areas to make the overall damage balance as uniform as possible throughout the converter refractory lining.[14, 15] **Table 3** shows the main damage factors and especially required properties for the specific converter lining areas.

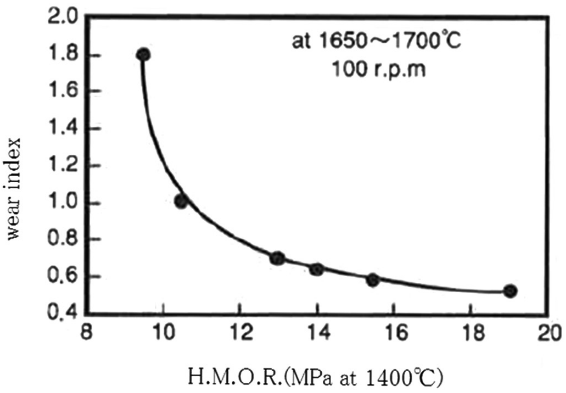


**Fig. 7 High temperature strength and abrasion resistance**

The converter throat and cone have damage problems, such as gas phase oxidation, physical impact during deslagging, and cracks due to the thermal expansion of the barrel. The dislodgment of bricks is prevented by such measures as adding SiC as an antioxidant, employing anchors driven into the steel shell to secure the bricks, and using metal cases for fusion bonding.

Damage of the tap hole sleeve is dominated by abrasion by molten steel flow and is considered to be accelerated by repeated heating and cooling during operation and by gas phase oxidation. The durability of the tap hole sleeve is being improved by adjusting the antioxidant addition and increasing the hot modulus of rupture.

Slag corrosion is dominant in the slag line, trunnion, and steel bath areas. Improvements have been made, such as densification by changing the particle size composition and binder type, suppression of structural deterioration due to cyclic thermal loading, and use of CaO-containing clinker with good slag coating properties.

The charging pad is subjected to mechanical impact when the hot metal is received from the hot metal ladle and when scrap is charged as a cold iron source. The MgO-C bricks for the charging pad area are increased in strength by decreasing the carbon content and increasing the metal addition content. Concerning spalling damage, another issue, reports are available about improving the spalling resistance by changing the binder and flake graphite types.[4, 5, 7]

Factors causing damage to the bottom tuyeres include graphite oxidation, slag corrosion, and spalling. Another factor is mechanical damage due to the back attack of the bottom blown gas and due to the flow abrasion by the molten steel. The bottom tuyere area is constructed of MgO-C bricks that have a higher graphite content than that of the bricks used in the walls. These bottom tuyere MgO-C bricks also have additives made to prevent the oxidation of graphite and to improve their strength.

In recent years, Nippon Steel Corporation developed the Multi-Refining Converter (MURC) process (**Fig. 8**) whereby dephosphorization and decarburization are continuously conducted in a single converter. As the new process became widely applied within the company, the penetration of low-basicity slag into refractories and the corrosion of the refractories by low-basicity slag exerted conspicuous effects on the MURC converter. The quality deterioration of iron ore, coke, and other steel raw materials increased the impuri-

**Table 3 Case of wear and required properties of each parts in BOF**

| Zone of BOF | Main cause of wear | Mainly required properties | | | |
|---|---|---|---|---|---|
| | | Corrosion | Oxidation | Abrasion | Spalling |
| Mouth, upper cone | Mechanical damage of skull removal<br>Oxidation by air | | ○ | ○ | ○ |
| Tapping hole | Oxidation by air<br>Abrasion by molten steel stream | | ○ | ○ | ○ |
| Slag line | Corrosion by slag | ○ | | | |
| Charging side | Mechanical damage by scrap charging<br>Abrasion by hot metal stream<br>Thermal spalling | | | ○ | |
| Trunnion side | Corrosion by slag<br>Abrasion by molten steel | ○ | | ○ | ○ |
| Lower cone | Corrosion by slag<br>Abrasion by molten steel | | | ○ | |
| Tuyere | Thermal spalling<br>Back attack by injected | | | ○ | ○ |

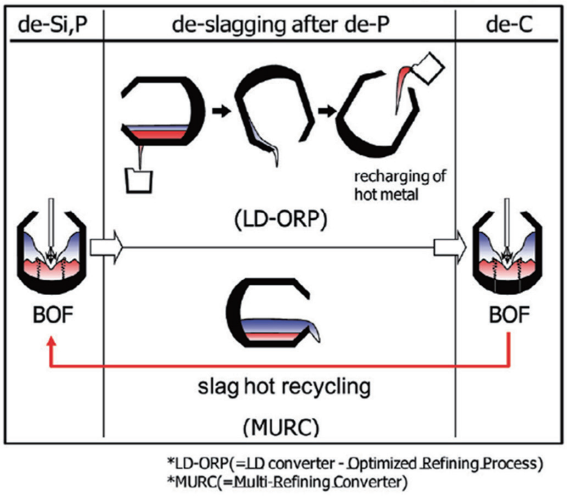


**Fig. 8 Converter-type hot metal pretreatment processes at Nippon Steel Corporation**

ties ([Si], [P], [S]) in the hot metal. This situation in turn exacerbated the operating severity of converters, increased the corrosion rate of MgO-C bricks, and urged the need for increasing the durability of MgO-C bricks.

## 6. Recent Technology Trends

### 6.1 Evaluation technology for simulating refractory corrosion in an actual converter

When we test MgO-C bricks in an actual converter, the technology to pre-simulate the actual converter on a laboratory level and to evaluate the actual durability of MgO-C bricks in the converter is very important in determining the material improvements to be made and the expected refractory cost, among other purposes. A recent study proposed the method of evaluating the corrosion resistance of MgO-C bricks by repeatedly heat treating and loading samples in order to reproduce the deterioration and corrosion of MgO-C bricks in the actual converter during long use. MgO-C bricks were thermally loaded by repeatedly heat treating them at a temperature of 1500°C or higher and at a temperature of 500°C or lower. This procedure physically loosened the structure of MgO-C bricks and structurally degraded the MgO-C bricks by the MgO-C reaction (**Fig. 9**). The proposed method reproduces well the structural deterioration of MgO-C bricks in an actual furnace. The simulated durability is shown to correspond well with the actual durability of MgO-C bricks.[16]

### 6.2 Technology for suppressing MgO-C reaction

As described above, the structural deterioration of MgO-C bricks by the MgO-C reaction is considered to greatly contribute to the wear of the MgO-C bricks. In recent years, technology has been developed for suppressing the MgO-C reaction by changing the particle size composition of MgO-C bricks. Reducing the reaction area between the magnesia clinker and the carbon material is also effective in suppressing the MgO-C reaction. Reducing the amount of 0.1 mm and finer particles in the magnesia clinker is reported to suppress the structural deterioration of MgO-C bricks due to the MgO-C reaction and to improve the corrosion resistance of MgO-C bricks (**Fig. 10**).

### 6.3 Reduction of graphite content and improvement of spalling resistance

In recent years, reduction in the graphite content of MgO-C bricks has been investigated from the viewpoint of suppressing the decrease in durability by eliminating the oxidation of graphite and from the viewpoint of reducing the heat loss. The graphite content reduction improves the corrosion resistance and decreases the thermal conductivity. As a result, the heat loss is reduced[17] but the spalling resistance is also reduced. Various efforts have been made to improve the spalling resistance of MgO-C bricks.

A study[18] is reported that improved the spalling resistance of low-graphite MgO-C bricks by covering the magnesia clinker with tar pitch. Also, technology is under development for sharply reducing the carbon addition content while maintaining the spalling resistance of MgO-C bricks by adding carbon nanoparticles of a few nanometers to a few tens of nanometers.[19]

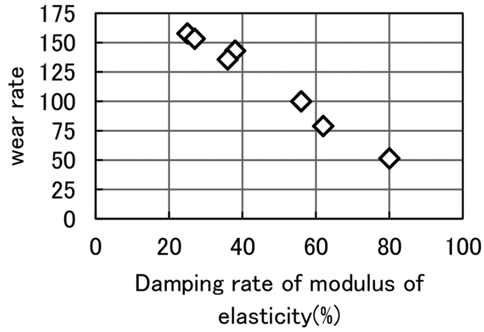


**Fig. 9 Damping rate of modulus of elasticity and wear rate**

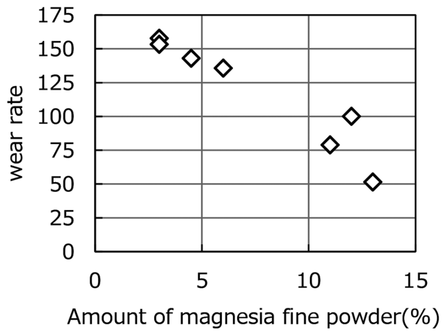


**Fig. 10 Magnesia fine powder and wear rate**

## 7. Conclusions

We have described MgO-C bricks mainly from the viewpoints of making them and using them in converters. The operating pattern and life of converters have evolved with the development of converter lining refractories. In recent years, the MgO-C bricks for converters have technologically matured, but examples have been reported whereby the durability of MgO-C bricks has been greatly improved by the various initiatives described above. We are required to continue our further efforts to improve the refractory technology and achieve technology innovations to lead to the further evolution of the steelmaking processes.

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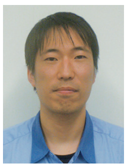


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