Various Technologies to Suppress Alumina Clogging for Submerged Entry Nozzle

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Abstract

One of the major issues with submerged entry nozzles (SEN) used in the continuous casting process is alumina clogging. Alumina clogging occurs through a complex process in which several chemical reactions and physical interactions take place simultaneously. In order to prevent alumina clogging, suitable SEN application in terms of material chemistry as well as geometric design is essential. In this article, features of our four material types and two shape designs, which suppress clogging suppression, and their application results are described.

1. Introduction

The submerged entry nozzle (SEN) is one of the functional refractories that distributes molten steel from the tundish to casting mold while creating a desirable steel stream in terms of steel product quality and production efficiency. Fig. 1 shows the steel flow path from tundish to casting mold. The inner geometry and port design of SEN are optimized for each casting condition to archive a suitable flow pattern in the mold.

Frequently, alumina clogging occurs on the surface of SEN bore and / or outlet port according to steel refining treatment. It is one of the major factors limiting the service life of SEN since severe alumina clogging

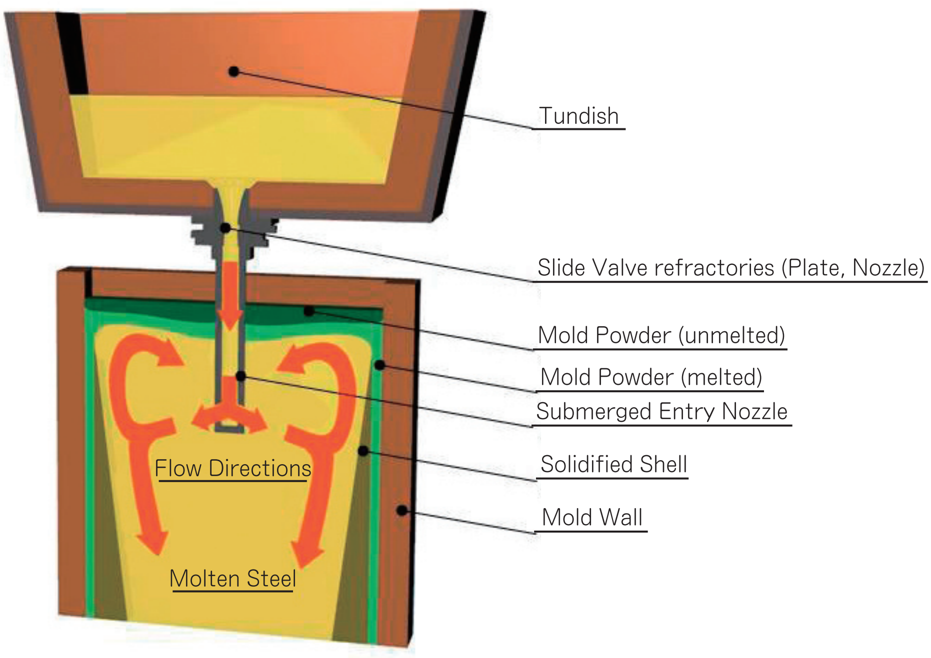

Fig. 1 Shematic image of the mold.

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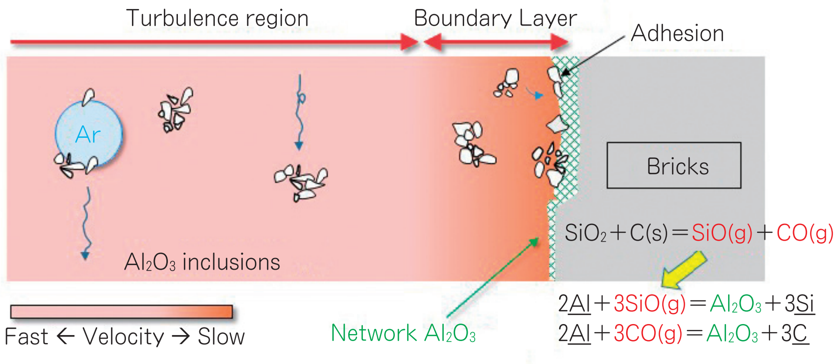

Fig. 2　Schematic image of alumina clogging.

reduces steel productivity due to throughput reduction and increased risk of steel defects caused by changing the flow pattern in the mold. Therefore, alumina clogging increases refractory consumption as well as probability of steel slab treatment or reproduction, resulting in an increase in excessive consumption of natural resources and energy. Thus, extra CO_2 is emitted.

As described above, suppressing alumina clogging in SEN has a large effect on improving not only the durability of SEN, stable production of steel, and improvement of steel quality, but also the reduction of waste and the minimization of resources and energy consumption. In this report, our technologies which can suppress alumina clogging are introduced.

2.　Mechanism of Alumina Clogging and Concepts of Countermeasures

2. 1　Mechanism of Alumina clogging

There have been many papers and reviews on the mechanism of alumina clogging[1-3], and they can be summarized as shown in Fig. 2.

Alumina clogging is a complex process that consists of network alumina and clusters of alumina inclusions and it often contains molten steel droplets. Of these, the network alumina is generated on the surface by the reaction of Al in the molten steel with gases such as SiO and CO (Eq.1) produced by the reaction between SiO_2 and C in the refractory at high temperatures (Eq.2, 3).

$$SiO_2(s)+C(s)\rightarrow SiO(g)+CO(g) \quad \cdots\cdots \quad \text{Eq.1}$$
$$3SiO(g)+2\underline{Al}\rightarrow 3\underline{Si}+Al_2O_3 \quad \cdots\cdots \quad \text{Eq.2}$$
$$3CO(g)+2\underline{Al}\rightarrow 3\underline{C}+Al_2O_3 \quad \cdots\cdots \quad \text{Eq.3}$$

On the surface of this network structure, aggregate of alumina inclusions suspended in molten steel attaches with a small fraction of liquid steel layer by layer to form an alumina clogging. The movement of the inclusion within the molten steel is influenced by the surrounding molten steel flow. Theoretically, while the molten steel flow flowing down the SEN inner bore is in a turbulent state, a boundary layer with a slower flow velocity is formed near the refractory surface. In this condition, the inclusions within the boundary layer move toward to the refractory surface due to the velocity gradient of the molten steel flow. It is known that the boundary area tends to be developed in areas where the flow is stagnant. On the other hand, agitation of the flow by introduction of specific inner geometry and/or Ar gas purging suppresses the development of the boundary layer.

When the alumina clusters within the boundary layer come into contact with the refractory surface, it is easy for them to become fixed on the refractory surface if it exhibits poor wettability to the molten steel. In particular, it is known that the rougher the refractory surface is, the poorer the wettability to molten steel becomes. On the other hand, when the surface of the refractory shows good wettability to the molten steel, the approaching alumina inclusions do not touch the surface since lower surface energy is achieved for the status of which liquid steel covers refractory surface.

2. 2　Concepts of suppressing Alumina clogging

As mentioned above, alumina clogging involves chemical and physical factors. In order to suppress alumina clogging, the measures shown in Fig. 3 are taken for each usage condition[4,5]. Technologically, measures to suppress alumina clogging can be classified into three categories. The first one is anti-clogging materials installed in the SEN inner bore. We have four compositions of anti-clogging materials (①−④). The second one is to optimize geometry to achieve desirable steel flow. According to intensive investigation, we obtained two types of geometries (⑤−⑥) as anti-clogging shapes. The last one is

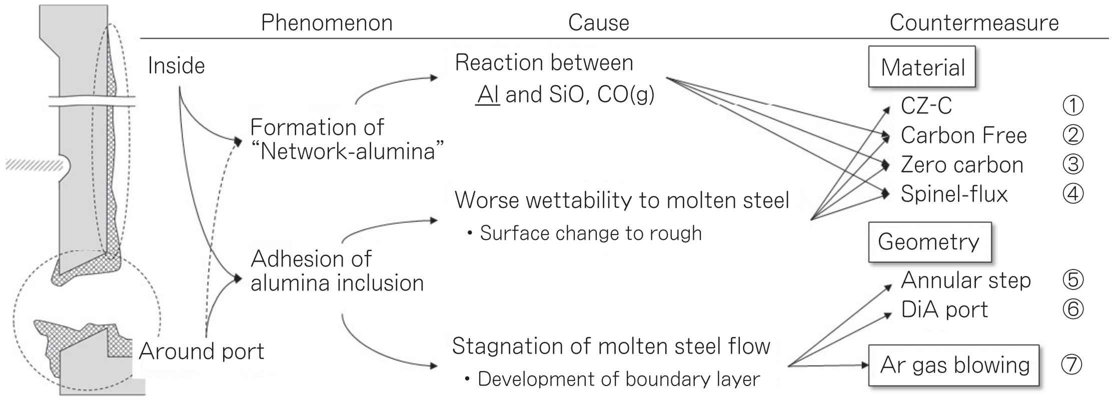

Fig. 3 Countermeasures of alumina clogging.

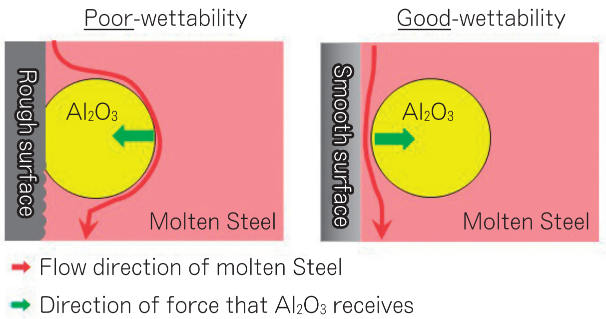

Fig. 4 Behavior of alumina inclusion near refractory surface.

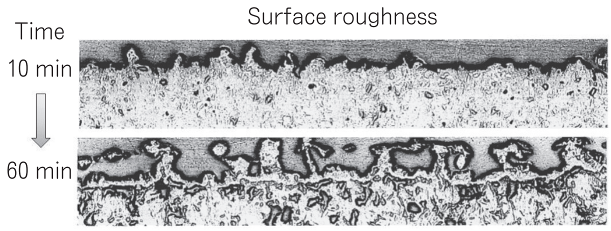

Fig. 5 Surface roughness change of refractory dipped into molten steel.

blowing an appropriate amount of Ar gas from the refractory materials such as SEN and the tundish upper nozzle on the upstream side of SEN (⑦). While every single measure is effective for suppressing alumina clogging, combined application of multiple measures from each category enhances the effect. In the following section, the anti-clogging technologies are described individually.

3. Material Measures and Actual Results

3. 1 CZ-C (①)

CZ-C material, which consists of calcium zirconate ($CaO \cdot ZrO_2$) and graphite, forms a dense layer on the surface with good wettability to molten steel by the reaction with inclusion components such as Al in the molten steel[6]. Fig. 4 shows the difference in alumina inclusion behavior according to the refractory surface wettability to molten steel

When an alumina cluster attaches on the poor-wettable surface, the molten steel flow that passes near the refractory surface changes its route to the inner side of the inclusions. Hence, attractive force is applied to the inclusions. Conversely, in the case of a refractory surface that shows good wettability, molten steel keeps contact flow on the surface even if an inclusion attaches on the refractory surface. Therefore, the inclusion is easily washed away from the refractory surface without adhesion.

Although CZ-C is extremely effective for suppressing alumina clogging, excessive reactions take place with specific steel compositions, resulting in considerable corrosion. In addition, if the flow velocity of the nozzle inner bore is fast during high-throughput operation, CZ-C may be washed away and the clogging suppression effect may be lost. In this way, CZ-C material is susceptible to operating conditions.

3. 2 Carbon free (②)

When carbon containing refractories contact molten steel, carbon exposed on the surface dissolves into the molten steel, resulting in a rough surface condition. Fig. 5 shows the change in surface roughness after immersing alumina graphitic material in molten steel for a certain period of time.

Carbon located in refractories reacts with the SiO_2 component and generates SiO and CO gas. These gases

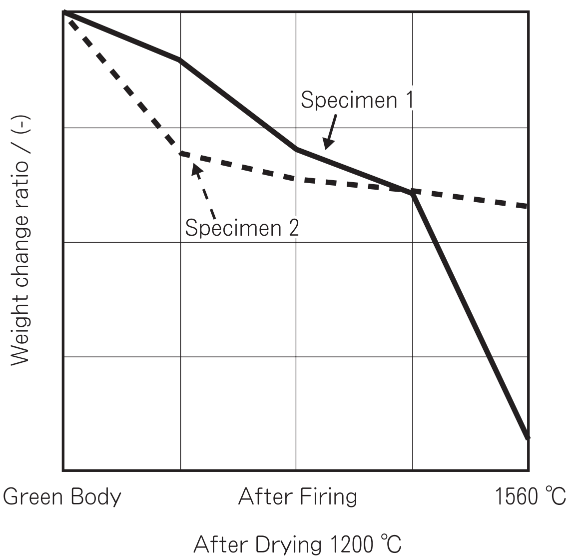

Fig. 6　Comparison of weight change.

move to the refractory surface and react with the Al in the molten steel to form network alumina on the refractory surface. Since this reaction promotes surface roughness deterioration, the wettability of the surface becomes worse, making it easier to promote alumina clogging.

Since carbon free materials do not include carbon raw materials, the surface roughness deterioration due to the dissolution of graphite in molten steel doesn't take place and SiO and CO gas are less likely to be generated. This makes it possible to maintain a smooth refractory surface state during casting in its initial. Therefore, carbon free materials are widely used at present because they can enhance the effect of suppressing alumina clogging by combination of annular step geometry and/or Ar gas blowing. This technology can be used for a wide range of casting conditions.

3. 3　Zero carbon (③)

Zero carbon material is a new material series that advances the concept of carbon free material. Carbon free material inevitably contains a small amount of residual carbon introduced by using phenolic resin as a binder. In practical operation, reduction of alumina clogging, extension of SEN service life and improvement of steel quality have been realized by application of the previously described carbon free material by reducing residual carbon as much as possible[7]. However, since the binder system still uses phenolic resin, it can be inferred that the reaction between the residual carbon and the SiO_2 aggregate generates a small amount of CO and SiO gas that oxidizes the Al in the molten steel. Thus, zero carbon material has been developed.

Zero carbon material is produced by using inorganic binder. Since its residual coal is zero, CO and SiO gas never are generated at high temperatures. For the sake of evaluation of the effectiveness, two samples consisting of the same aggregate material using different binders, phenolic resin (Specimen 1) and inorganic binder (Specimen 2), were prepared. These two specimens were subjected to mass change evaluation through drying and firing in the manufacturing process followed by laboratory experimental heating at 1200 ℃ and 1560 ℃. Those temperatures are equivalent to preheating and steel casting in actual applications, respectively. The results are shown in Fig. 6. Specimen 1, to which phenolic resin was added as a binder, showed larger weight loss in the 1560℃ treatment. This suggests that gas species was generated and escaped. On the other hand, Specimen 2, to which inorganic binder was used, showed a large mass loss until firing, while the weight loss at high temperature was slight, suggesting that no gas species was generated.

SENs, to which carbon free and zero carbon materials were used as the inner liner were tested at billet CC at steelworks A. Both were used for about 5 hours in the same tundish. Fig. 7 shows the microstructures of the materials after use. While no significant alumina clogging was observed in either SEN, the conventional carbon free material showed higher degree of porousness in the reaction layer and clogging layer associated with a large amount of molten steel droplets and Ca-containing component. On the other hand, it is clear that the working surface of the zero carbon material showed a smooth surface covered with the liquid phase with small amount of metal droplets and Ca-containing component.

This phenomenon indicates that the structure of the zero-carbon material makes molten steel and slag penetration difficult thanks to the suppression of internal gas generation. If it is applied to specific steel grades such as ultra-low carbon steel, which is prone to alumina clogging, a clear difference in clogging suppression effect is expected to be observed.

3. 4　Spinel-flux (④)

Spinel-flux material is a new carbon free material that has excellent wettability to molten steel, as much as that of CZ-C, with less susceptibility of durability to operating conditions. In this material, the flux component melts adequately with the heat from the molten steel and covers the refractory surface, improving wettability to the molten steel so as to suppress the alumina clogging[8]. Furthermore, thanks to the carefully optimized spinel aggregate arrangement, it is possible to prevent the

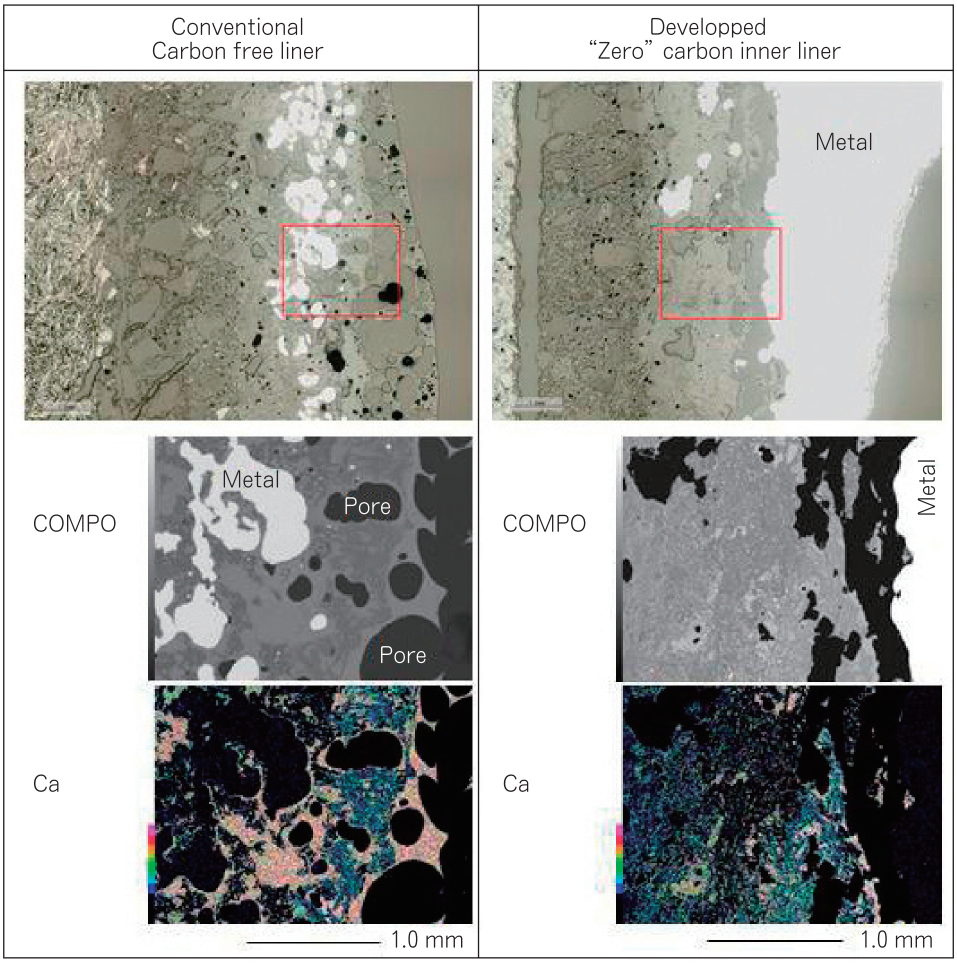

Fig. 7 EPMA analysis of "Zero" carbon inner liner after use.

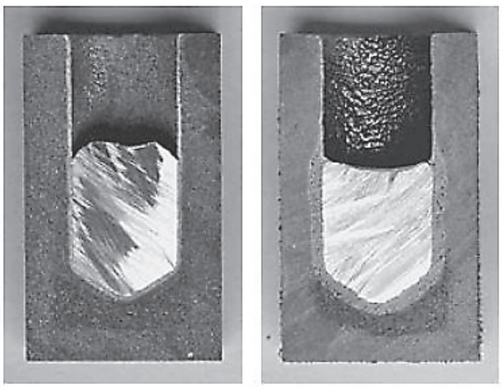

Fig. 8 Crucible test results.

spinel-flux material from excessive melting. This material can be applied to a wide range of steel grades from those prone to alumina clogging to those prone to refractory corrosion. Hence, it eliminates the on-site complexity of selection according to steel grade.

The effectiveness of improving wettability to molten steel by adding a flux component was validated experimentally as follows. Two kinds of crucibles, composed of spinel carbon free material and spinel-flux material, were prepared. Steel pieces were put into the hollows of the crucibles followed by heating to melt the steel. After cooling, the crucibles were cut vertically together with the resolidified steel and the surface condition of the crucibles and the meniscus shapes of resolidified steel were compared. The result is shown in Fig. 8

The spinel-flux crucible showed a glassy surface and it was clarified that a low melting temperature substance was formed on the refractory surface. In addition, the meniscus shape of resolidified steel in the spinel carbon free material had a large convex shape, while the spinel-flux material had a concave shape. This difference indicates that the spinel-flux material exhibits better wettability to molten steel.

The actual results applying spinel-flux material to SEN is as follows. As a result of applying it to the SEN of a

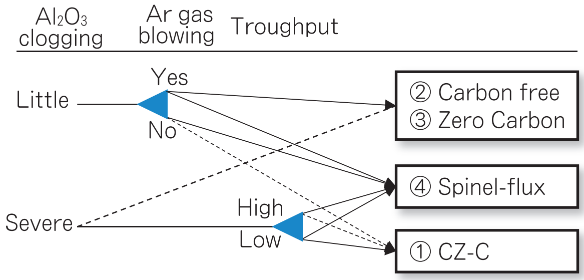

Fig. 9　Application conditions for anti-clogging materials.

slab caster at steelworks B, the frequency and degree of abnormal opening of the slide valve plate due to alumina clogging decreased compared to the case of applying the conventional alumina-silica carbon free material. As a result of applying it to a single-hole type SEN in steelworks C's billet caster (used for 9 heats with total approximately 550 minutes in total casting time), only slight clogging was observed while the conventional SEN showed severe alumina clogging in its inner bore. Thus, it was concluded that the spinel flux material is applicable to a wide range of operating conditions.

3. 5　Method for using each anti-clogging material

Fig. 9 summarizes the application methods of the four anti-clogging materials listed above. If the alumina clogging is slight, favorable results can be expected by applying carbon free and zero carbon materials in combination with Ar gas blowing. On the other hand, in cases where Ar gas blowing is difficult or alumina clogging is severe, application of spinel-flux material or CZ-C material is considered to be an effective means. Especially, as mentioned above, CZ-C material has the best effect in terms of alumina clogging suppression, but it has a risk of disappearance during use. In particular, it is necessary to note the risk of the working time of CZ-C will being limited under operating conditions with high throughput. It is necessary to take the material distribution design into consideration according to usage conditions.

4.　Measures from Geometry and Actual Results

4. 1　Annular step geometry (⑤)

Originally, the annular step geometry shown in Fig. 10 was developed for the purpose of eliminating the biased flow in the nozzle generated by the throttle of the tundish plate. Additionally, in combination with Ar gas blowing, suppression of alumina clogging has also been confirmed[9].

This is because the annular step geometry suppresses development of a boundary layer by agitating the flow in the bore, and Ar bubbles supplied from the tundish nozzle improve the efficiency of capturing alumina inclusions from the molten steel. For the inner bore, the alumina clogging suppression effect can be enhanced by combination of annular step geometry and anti-clogging material. However, it may be difficult to use anti-clogging material around the outlet ports due to the complicated shape. For the above reason, there are cases in which a severe alumina clogging is observed around the outlet port, even if no alumina clogging is observed in the bore.

4. 2　DiA port (⑥)

The DiA (Different Angle) nozzle, which is newly developed, can suppress alumina clogging around the outlet port. The DiA nozzle is characterized by a design that

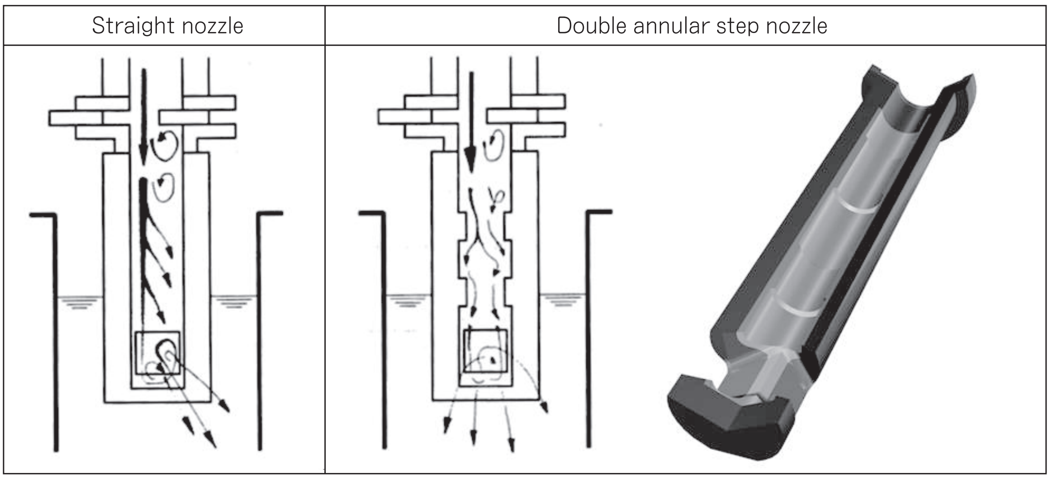

Fig. 10　Effect of annular step geometry.

differs from the conventional outlet port design concept, with the upper side of the port facing downward and the lower side facing upward[10]. This design creates an outlet flow that is discharged more evenly from the entire outlet port.

Fig. 11 shows the schematic shape and outlet flow pattern of the conventional port and DiA port. Fig. 12 shows the CFD calculation results for these areas. In the case of the DiA nozzle, the flow stagnation near the port upper and lower wall, which occurs in conventional nozzles, was not observed. Since flow stagnation promotes alumina clogging, it was expected that the DiA geometry would be effective in suppressing alumina clogging.

The DiA nozzle was evaluated on the slab caster of steelworks D. In the conventional nozzle that had been used in this caster, severe alumina clogging had been confirmed near the upper and lower part of the port. A sketch of state of alumina clogging in the conventional nozzle and the DiA nozzle is shown in Fig. 13. It was confirmed that the DiA nozzle significantly suppressed the alumina clogging. In this slab caster, decreasing steel defects caused by inclusion trapping has been reported by using the DiA nozzle[10]. The DiA nozzle can be adopted not only to optimize the initial flow pattern in the mold, but also to suppress large inclusion generation, and to maintain an ideal flow pattern without clogging. These effects will result in good casting slab quality.

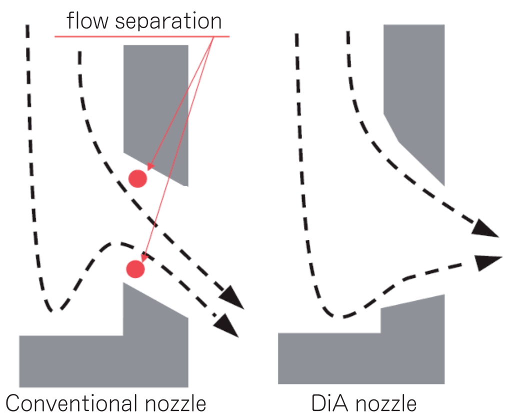

Fig. 11 Comparison of port designs and molten steel flow.

5. Conclusions

We reported on the latest technology and its application results regarding the material and design of a nozzle that

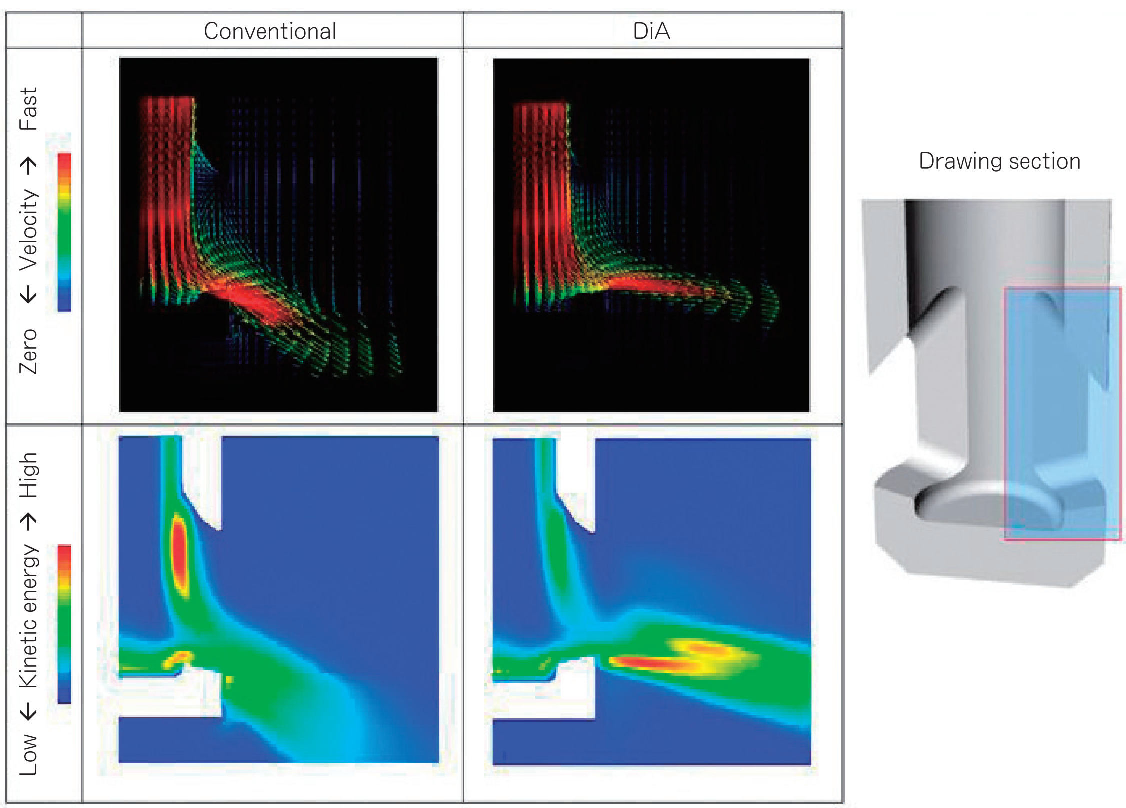

Fig. 12 Calculation results around outlet port.

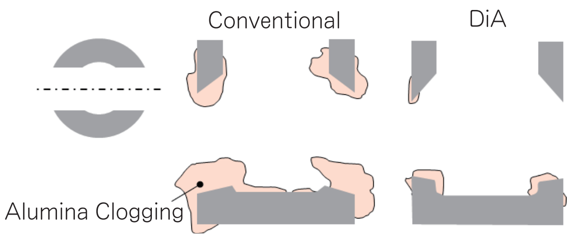

Fig. 13　Schematic drawing of alumina clogging around ports.

can suppress alumina clogging. We believe that suppressing alumina clogging is the SEN is an important topic from the viewpoint of not only improving SEN durability, promoting stable casting operation and improving steel quality, but also suppressing the excess use of resources and energy.

Based on the results of the alumina clogging suppression described in this article, we plan to make further improvements toward the establishment of a universal alumina clogging suppression technology that can be applicable to any casting conditions.

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