# Development of CaO-$Al_2O_3$ Based Mold Flux System for High Aluminum TRIP Casting

*Jung-Wook Cho[1], Kenneth E. Blazek[2], Michael J. Frazee[3], Hongbin Yin[2], Jeong Hyouk Park[4], Sang-Woon Moon[1]*
*1:Steelmaking Research Group, Technical Research Lab, POSCO, 2: ArcelorMittal Global Research-EC USA,*
*3:Global Metallurgy Marketing – S&B Industrial Minerals S.A., 4: Stollberg & Samil CO., LTD., South Korea*

**Abstract:** Today, the demands for Advanced High Strength Steels (AHSS) have gradually increased due to their ability to reduce vehicle weight as a means to save energy, reduce the environmental impact while simultaneously improving passenger safety. However, AHSS often require the addition of large amounts of alloying elements such as aluminum and this can make it difficult to cast sound slabs without surface defects. When casting high aluminum Transformation Induced Plasticity (TRIP) and Complex Phase (CP) grades, due to the reaction between aluminum in steel and silica in traditional lime-silica based mold powders, the viscosity and crystallization characteristics of the mold slag changes drastically, and deteriorates mold lubrication. Therefore, it is critical to limit the reaction between Al in steel and mold slag and at the same time to provide consistent and adequate mold slag in-use properties. This paper describes the development of non-traditional lime-alumina based mold fluxes which have the potential to reduce slag-steel interaction during casting of high aluminum TRIP steel grades. This work was carried out through a collaborative development program among POSCO Research Laboratories, ArcelorMittal Global R&D – East Chicago Center (ECC) and Stollberg (USA and South Korea). Several trial casts of 1.5% Al TRIP steel have been conducted on POSCO's research pilot caster to examine the performance of mold fluxes developed within this project. When the lime-alumina based mold powders were applied successfully, alumina pickup was reduced to less than 5% as compared to 15% alumina pickup for corollary trial casts using conventional lime-silica mold fluxes. The developed lime-alumna mold fluxes showed improved in-mold performance as indicated by enhanced lubrication and stable mold heat transfer, again compared to lime-silica powders. Cast slabs from the trials using these lime-alumina fluxes have periodic and sound oscillation marks and minimized defects.

**Key words:** Mold flux, Lime-alumina, Alumina pickup, Mold heat transfer, Lubrication

## 1. Introduction

It is well known that high concentration of aluminum in the steel is prone to react with $SiO_2$ and other less stable oxides than $Al_2O_3$ in the continuous casting mold, as shown below.

$$3(SiO_2) + 4[Al] = 3[Si] + 2(Al_2O_3) \quad (1)$$

$$3(MnO) + 2[Al] = 3[Mn] + (Al_2O_3) \quad (2)$$

These reactions usually lead to poor performance of mold flux such as decreased mold flux consumption, heavily sintered flux layer, intense off gassing and flaming. As a result, the change of the physical properties of mold slag deteriorates both the casting operation and the surface quality of cast slabs. For example, Blazek et al.[1)] reported various kinds of troubles and defects such as BOP (Break Out Prediction) alarms, transverse and longitudinal depressions, and so on.

Considerable efforts have been carried out to suppress the abrupt change of mold flux properties such as viscosity during high Al steel casting by optimizing the ratio of $CaO/SiO_2$ or $Al_2O_3/SiO_2$ for the conventional lime-silica based mold flux system. However, it is difficult to design an optimal composition due to constantly changing (usually increasing) viscosity with the progress of equation (1) in the lime-silica based mold flux system.[2)]

The authors have been developing lime-alumina based mold powders[1,3)] in an effort to replace the current lime-silica based powders for use on high aluminum TRIP steels by the joint research program among Stollberg, ArcelorMittal Research USA and POSCO. New mold flux should be chemically stable during casting with optimum consumption rate, and minimal surface cracking. To this end, casting trials for high aluminum TRIP steels were carried out to evaluate various lime-alumina based mold fluxes on POSCO's pilot continuous caster. This paper summarizes the results of the trials and the decisions made as to the future direction for this project

## 2. Pilot casting operation

To examine the performance of lime alumina mold fluxes, a series of tests have been carried out using a 10-ton scale pilot caster in POSCO, Pohang Works. The specification of the pilot caster is described in Table 1. The T-type (copper and constantan) thermocouples were embedded in the mold plate to measure mold temperature during casting. The total number of thermocouples was 124.

A total of eight pilot trials were carried out for 1.5% aluminum TRIP steel. The casting conditions were as follows:

- 950 mm width and 140mm thickness
- 0.9 m/min casting speed
- 40 °C superheat (aim of 1559 °C for the molten steel in the tundish)
- Oscillation frequency of 117 x casting speed and oscillation stroke of 6 mm (aim 1.4 of negative strip ratio)
- Aim steel chemistry of 1.45% Al with other elements to make TRIP properties

Table 1 Specification of the pilot caster

| | |
|---|---|
| Cast Type | Vertical Curved Type<br>Casting Radius 5 m, Machine Length 19.5 m |
| Slab Thickness | 60~140 mm (½ Scale of Commercial) |
| Slab Width | 600~1,000 mm (½ Scale of Commercial) |
| Cast Speed | 0.8~5 m/min |
| Ladle | Max 12 Tons |
| Tundish | 5 Tons |
| Mold Type | Parallel, Funnel, Chamfered Type |
| Oscillator | Hydraulic |
| Secondary cooling | Air-Mist |

For each casting trial, a total of 10 tons of steel was melted in an induction furnace. After adjustment of the temperature and chemistry, molten steel was delivered to casting position. Applied mold fluxes were fed into the casting mold at the beginning of casting. During casting operation, mold slags were frequently taken to examine the change of chemistry. In each face of the casting mold, the temperature and flow rate of cooling water were measured to calculate mold heat flux density. After each casting operation, the cast slab was cleaned by shot blasting to observe any surface defects and to measure the depth of oscillation marks and depressions on surface.

## 3. Results and Discussion

### 3.1 1st trials using lime-silica and lime-alumina based mold fluxes

The 1st trials consisted of five casts on the POSCO pilot caster. Based on extensive testing over several years, the following five mold fluxes were selected for the trials as shown in Table 2. Among the five mold fluxes, AM1 was selected because it is the current mold flux used on the ArcelorMittal caster to produce commercial heats of high aluminum TRIP steel. Therefore, AM1 represents the basis of comparison for the surface quality of the cast slabs and for the stability of the casting operation. A variation of AM1 was designed by adding some zirconia to decrease mold heat transfer and improve surface quality on the high aluminum TRIP steel, shown as AM2 in Table 2. The final three powders selected were the lime-alumina based powders developed.

**Table 2 Chemical composition and physical properties of mold fluxes for 1st trials**

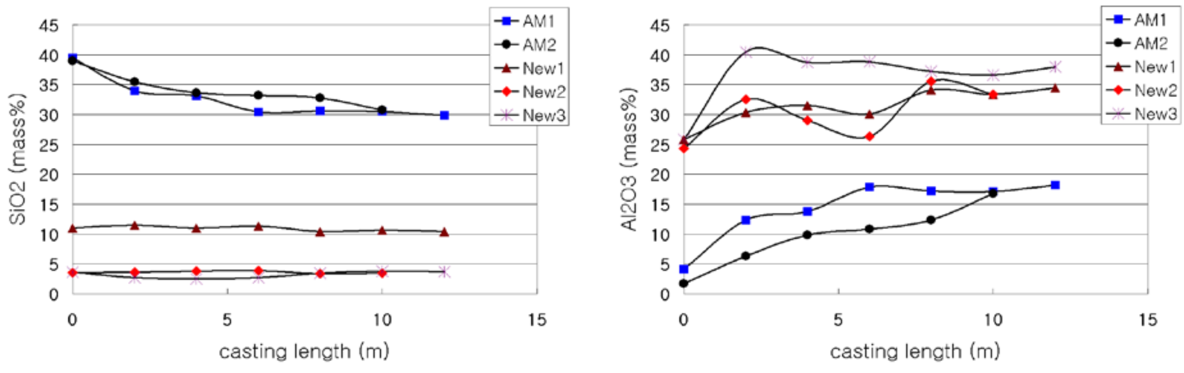
| Cast | Mold flux | Chemical composition (mass %) | | | | | | | | | Visco. (1300℃) | Break temp. (℃) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | CaO | SiO2 | Al2O3 | MnO2 | Na2O | F | B2O3 | Li2O | ZrO2 | | |
| #1 | AM1 | 19.9 | 36.4 | 3.8 | 6.6 | 11.1 | 9.8 | - | 2.1 | - | 1.80 p | 935 |
| #2 | AM2 | 19.3 | 35.4 | 1.5 | 6.2 | 10.5 | 9.3 | - | 3.0 | 3.5 | 1.47 p | 920 |
| #3 | NEW1 | 28.0 | 9.9 | 27.2 | - | 9.5 | 9.1 | - | 4.2 | - | 1.45 p | 1070 |
| #4 | NEW2 | 30.7 | 2.2 | 25.1 | - | 12.3 | 15.1 | 5.4 | 3.1 | - | 0.75 p | 1060 |
| #5 | NEW3 | 32.0 | 2.3 | 26.2 | - | 7.4 | 13.9 | - | 6.4 | - | 0.77 p | 925 |

All the trials were made under steady state casting speed conditions except for cast #5 on which the NEW3 lime-alumina based mold flux was used. During this trial, there was a concern about a breakout due to the sticking in casting mold and therefore the casting speed was reduced to 0.6 m/min when about 7 meters of steel had been cast. The final chemistries for all heats are summarized in the Table 3. All of the compositions are in the low mold heat transfer region of the hypo-peritectic area in the phase diagram for this steel grade. Melting of the heats was done in an air induction furnace and therefore the nitrogen content could not be controlled easily. The nitrogen content was from 100 to 300 ppm, which was much higher than commercial TRIP steels produced at ArcelorMittal USA based on a BOF-LMF route.

Table 3 Steel compositions for 1st trials

| Cast | Al (mass%) | N(ppm) |
|---|---|---|
| #1 | 1.41 | 189 |
| #2 | 1.29 | 96 |
| #3 | 1.42 | 139 |
| #4 | 1.46 | 299 |
| #5 | 1.53 | 96 |

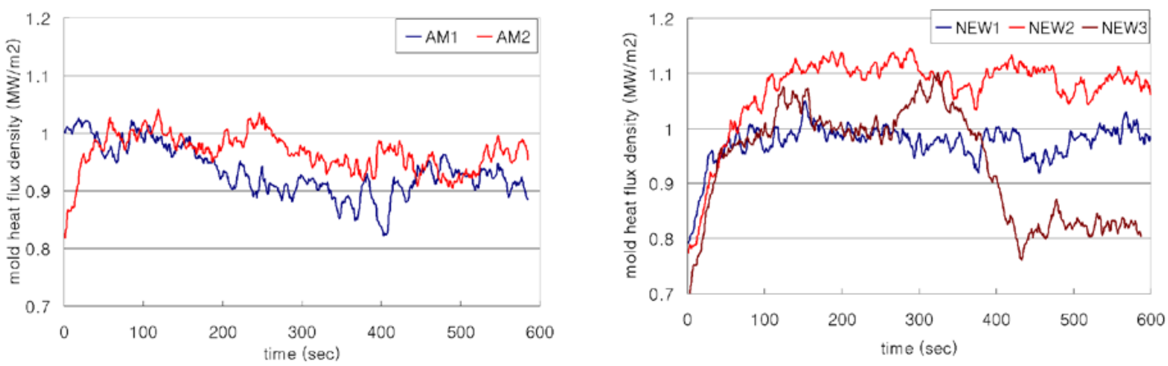
Molten slag samples were obtained every two meters of casting length, which is roughly equivalent to every 135 seconds. The variation in slag chemistry for the five trials is shown in Figure 1. For the conventional lime-silica fluxes, AM1 and AM2, the silica content declined by nearly 10 % while the alumina content increased from about 5 to 20 %. The amount of silica reduction was less than 3 % for the three lime-alumina fluxes while the alumina content increased by about 10 %. Overall, the increase of alumina exceeds the expectation from equation (1). In this study, the alumina analyses were carried out on the assumption that all the ionic aluminum come from alumina. However, Yin et al.[4] reported that a large amount of aluminum nitride can easily form during continuous casting of the same steel grade. Therefore, considering comparatively larger nitride contents of this study than any commercial plants, some of the ionic aluminum identified in the analyses is believed to be aluminum nitride.




**a) $SiO_2$** **b) $Al_2O_3$**

**Fig. 1 Mold flux compositions change during 1st casting trials**

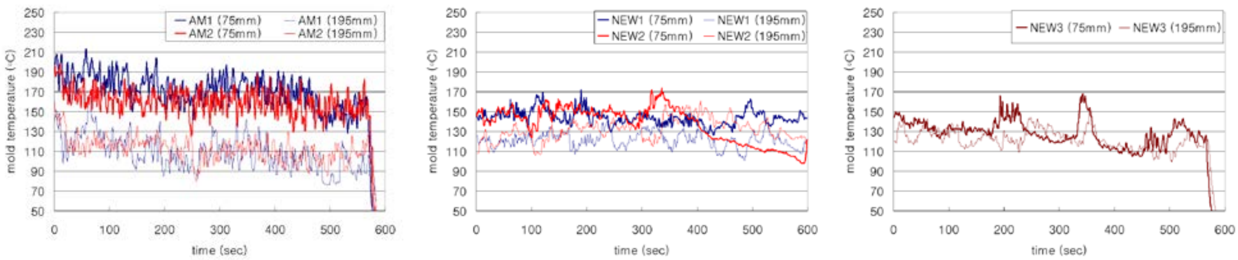
Overall mold heat transfer rates on the loose side of the broad face mold plate are shown in Figure 2. During casting using conventional lime-silica mold fluxes, a fade in mold heat transfer rate is noted for both the narrow and wide faces of the mold, which is the same behavior noted on the commercial caster for this mold powder. This is attributed to the increase of crystallization temperature of mold slag film due to the change in composition by reaction of equation (1). The amount of mold heat transfer rate for lime-alumina fluxes is virtually the same, at 1.0~1.1 $MW/m^2$ for the whole casting operation except when casting with NEW3 at reduced speeds. This is consistent with the negligible change of silica for the lime-alumina mold fluxes as shown in Figure 1.




**a) Lime-silica mold fluxes** **b) Lime-alumina mold fluxes**

**Fig. 2 Mold heat transfer rate during 1st casting trials**

Among a total of 124 thermocouples embedded in casting mold, two thermocouples in the center of the mold broad face are selected to show the degree of stability in mold heat transfer during casting as can be seen in the Figure 3. The two thermocouples were located 75mm and 195mm below the meniscus respectively. There is a considerable difference of temperature between the upper and the lower thermocouples for the trials using lime-silica fluxes. Also, the fluctuation of temperature from these thermocouples is significant, which is believed to be due to the change of mold slag composition by Equation (1). The behavior of mold temperature is drastically changed when lime-alumina based mold fluxes are used. In comparison with the mold temperature when the lime-silica mold fluxes are used, the temperature difference between the upper and the lower thermocouples is only a little more than 10 degree Celsius and the fluctuation of temperature is insignificant. This is an indication that the mold heat transfer rate near the meniscus has been sharply decreased by some means which is most likely the presence of the opaque crystalline slag film acting as an added thermal resistance to heat transfer.




**a) Lime-silica mold fluxes** **b) NEW1 and NEW2 mold fluxes** **c) NEW3 mold flux**

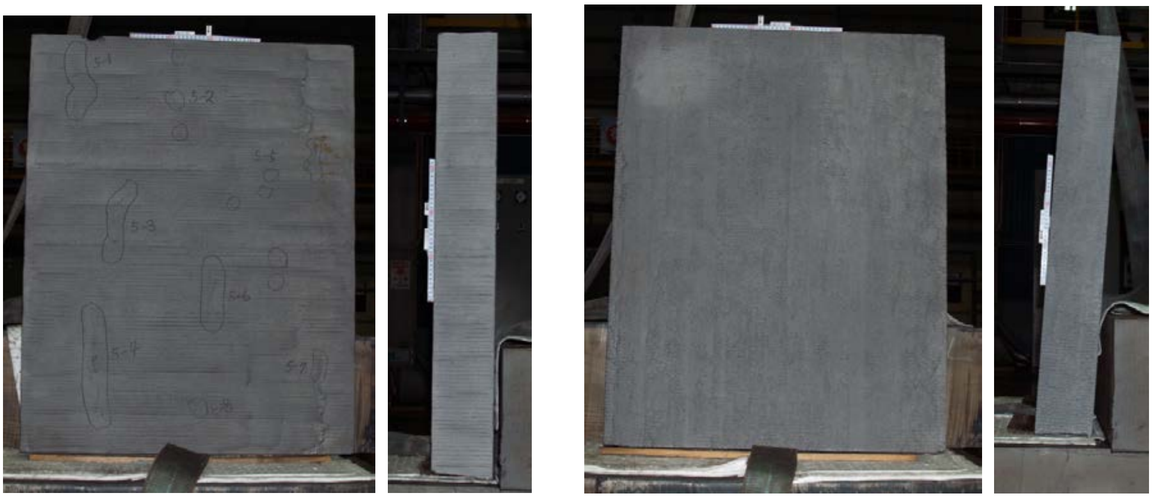
**Fig. 3 Mold temperature behavior during 1st casting trials**

A few examples of the as-cast slab surface quality for the trials are shown in Figure 4. There were many horizontal and vertical depressions which contained open cracks on the surface of the slab cast using lime silica based mold fluxes. The oscillation marks were very distinct and straight across the surface of the slab. Also, the surface did not have drag marks indicating sufficient lubrication during casting. When the lime-alumina mold fluxes were applied, the surface appearance of cast slabs was entirely different from the trials of lime-silica fluxes. Virtually all the longitudinal and transverse depressions have been eliminated by application of lime-alumina based mold fluxes as can be seen in Figure 4-b). This is most likely due to the significant decrease in mold heat transfer rate near the meniscus. However, the oscillation marks were not as distinct and straight as seen in the cast trials with lime-silica mold fluxes. Also, the surface has drag marks which are the indication of insufficient lubrication.

The trials at POSCO have indicated that the POSCO pilot caster produces similar surface quality when casting high aluminum TRIP steels with AM1 mold flux as produced on ArcelorMittal's commercial caster. The application of the lime-alumina mold fluxes prevented the occurrence of severe surface cracks on cast slabs by stabilizing the mold heat transfer at the initial stage of high aluminum TRIP steel casting. However, they do not provide the same level of lubrication as a commercial lime-silica based mold flux, AM1. The best surface quality was produced with the NEW3 followed by NEW1. Among the lime-alumina based mold fluxes, NEW2 had the worst surface quality. Overall, the lubricating properties of all these lime-alumina mold fluxes must be improved before they are used on a commercial casting of high aluminum TRIP steels.

### 3.2 $2^{nd}$ trials using improved lime-alumina based mold fluxes

A total of three trial casts were carried out during the $2^{nd}$ set of trials using three different lime-alumina based mold fluxes as shown in Table 4. The design of these new mold fluxes was to improve lubrication which was determined to be the biggest issue with the initial lime-alumina compositions tested in the $1^{st}$ trials. An intensive investigation has been carried out[1,3] to examine the physical properties such as viscosity and solidification temperature to develop promising candidates for future mold flux trials. To improve lubrication of lime-alumna base mold fluxes, the following three factors have been optimized; 1) lime to alumina ratio, 2) amount of lithium oxide substituted for sodium oxide, 3) concentration of boron oxide. All other casting conditions in $2^{nd}$ trials are largely the same as those in $1^{st}$ trials except for the increase of the distance between embedded thermocouples and mold hot faces, which lowered the mold temperatures considerably compared with the $1^{st}$ trials.



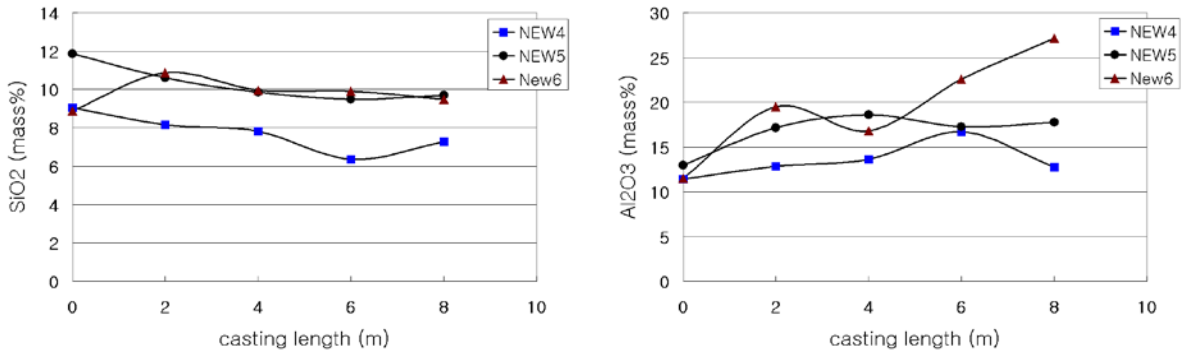
**a) Cast #2 with mold flux AM2** **b) Cast #3 with mold flux NEW1**

**Fig. 4 Typical TRIP slab surface quality obtained during $1^{st}$ casting trials**

**Table 4 Chemical composition and physical properties of mold fluxes for $2^{nd}$ trials**

| Cast | Mold flux | Chemical composition (mass %) | | | | | | | | | Visco. (1300℃) | Break temp. (℃) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | CaO | SiO2 | Al2O3 | MnO2 | Na2O | F | B2O3 | Li2O | ZrO2 | | |
| #6 | NEW4 | 37.9 | 9.0 | 11.4 | - | 9.0 | 8.9 | 16.0 | 4.9 | - | 0.55 p | 900℃ |
| #7 | NEW5 | 42.6 | 11.9 | 13.0 | - | 4.8 | 9.3 | 10.8 | 4.9 | - | 0.84 P | 975℃ |
| #8 | NEW6 | 37.8 | 8.9 | 11.5 | - | 1.0 | 8.1 | 15.0 | 6.2 | - | 0.38 p | 875℃ |

The compositional change of mold slag is shown in Figure 5. The reduction of silica by the reaction in equation (1) was less than 5% for all three trials. However, the increase of aluminum ion exceeded the expectation from equation (1), which may be due to reduction of $B_2O_3$ or formation of aluminum nitride in the continuous casting mold. The mold fluxes tested were chemically stable as a whole. Figure 6 shows the behavior of mold heat transfer on a broad face of the casting mold. The mold heat transfer is most stable during the trial using NEW4 mold flux while some fluctuation was observed with NEW5 and NEW6. In addition, average mold heat flux rate of NEW6 mold flux was larger than the other two trials. Figure 7 shows the mold temperatures 75 mm and 195 mm below the meniscus at the center of a broad face during trials. The average mold temperature is largest on the trials using NEW6 mold flux, followed by NEW4 and NEW5. It is worthy to note that the mold temperature has been gradually decreased for the trials using NEW4 and NEW5 mold fluxes, which implies that the crystallization of mold slag film were in progress during casting.




**a) $SiO_2$** **b) $Al_2O_3$**

**Fig. 5 Mold flux compositions change during 2nd casting trials**

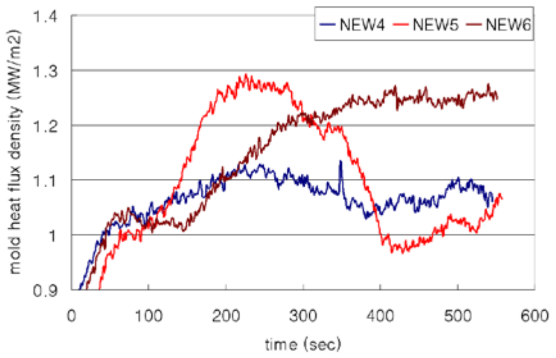
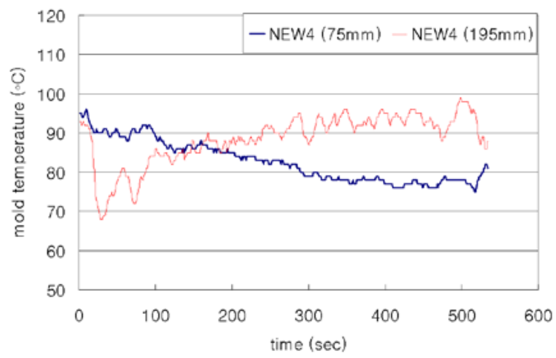
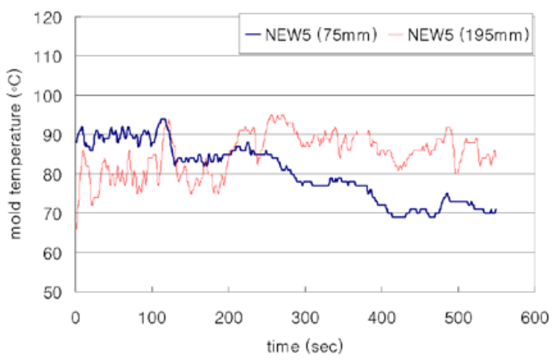
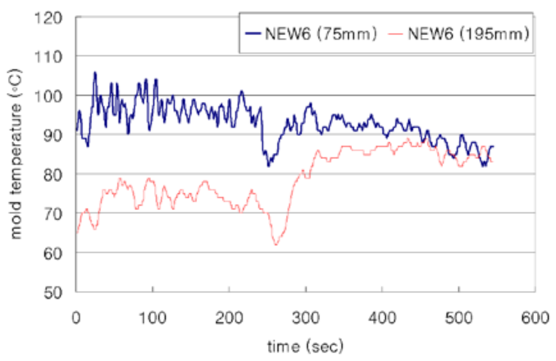



**Fig. 6 Mold heat transfer rate during 2nd casting trials**




**a) NEW4 mold flux**

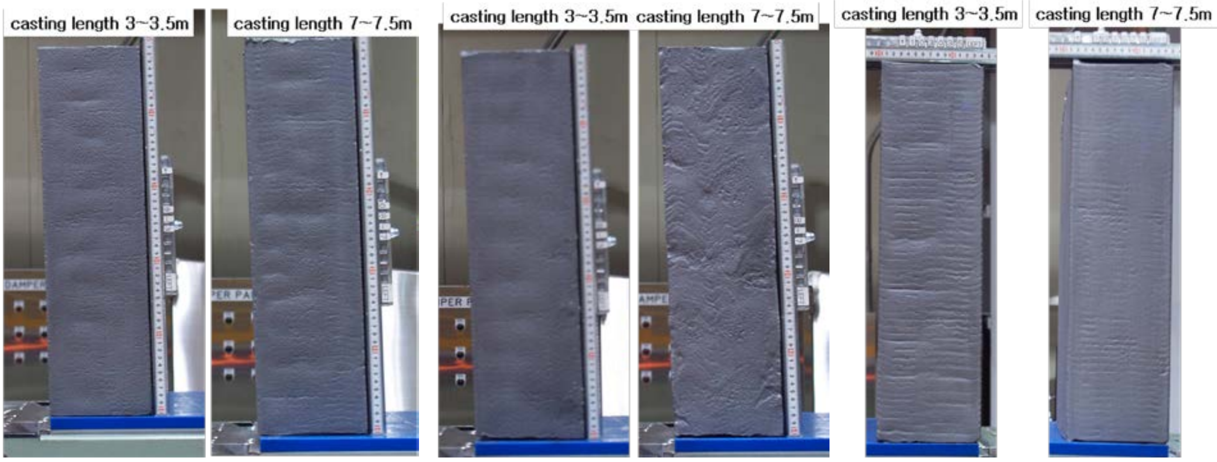


**b) NEW5 mold flux** **c) NEW6 mold flux**

**Fig. 7 Mold temperature behavior during 2nd casting trials**

There is a strong correlation between mold heat transfer behavior and the appearance of cast slabs, as can be seen in Figure 8. For the trials using NEW5 and NEW4 mold fluxes, drag marks appeared on the slab surface due to lack of lubrication. This was especially observed for the latter half of the slab cast using NEW5 mold flux as seen in Figure 8-b). On the contrary, slabs from the trial using NEW6 mold flux didn't show severe drag marks but revealed many depressions. The crystallization characteristics of mold slags are the key to understanding the different behavior of mold heat transfer and hence the slab appearance. It is well known that a crystalline slag film has larger thermal resistance and poor lubrication in the casting mold. Therefore, application of highly crystalline mold fluxes usually minimizes depressions on the cast slab surface and hence cracks while the lack of lubrication can easily yield the drag marks and the abrupt fluctuation of mold temperature due to the breakage of slag film, as can be seen in Figure 8-b). In this context, it seems that NEW5 mold flux has the strongest tendency of crystallization, followed by NEW4 and then NEW6 mold flux.




**a) Cast #6 with mold flux NEW4** **b) Cast #7 with mold flux NEW5** **c) Cast #8 with mold flux NEW6**

**Fig. 8 Typical TRIP slab surface quality obtained during 2nd casting trials**

The difference of crystallization may arise from the amount of boron oxide, sodium oxide and lithium oxide in mold fluxes. Boron oxide is a strong glass former and therefore suppresses crystallization. Also, alkaline metal oxides such as $Na_2O$ and $Li_2O$ can restrain the crystallization of lime-alumina slag system by increasing the incubation time for crystalline growth[5)]. Because of smaller $B_2O_3$ and $Na_2O$ in NEW5 mold flux, it is believed to be more crystalline than NEW4. The larger drag marks and smaller mold temperature are attributed to the accelerated crystallization of NEW5 mold flux. The largest mold heat transfer rate using NEW6 mold flux may arise from the more glassy slag film due to the largest $Li_2O$ which can greatly retard the crystallization of mold slag.

The overall evaluation of mold fluxes and cast trials can be seen in Table 5. As both the castability and surface quality are by far the best among three mold fluxes tested, NEW4 mold flux is believed to be a successful candidate for the commercial casting of high aluminum TRIP steel. Also, it is highly desirable to improve the behavior of lime-alumina base mold flux by controlling the degree of crystallinity of the slag film.

**Table 5 Evaluation of the performance of mold fluxes for $2^{nd}$ trials**

| Item | NEW4 | NEW5 | NEW6 |
|---|---|---|---|
| Heat flux density ($MW/m^2$) | Wide face: 1.0~1.2<br>Narrow face: 0.8~1.0 | Wide face: 0.9~1.3<br>Narrow face: 0.8~1.2 | Wide face: 1~1.25<br>Narrow face: 1~1.25 |
| Mold temperature fluctuation | small | medium | large |
| Apperance of slab surface on wide face of slab | Many shallow depressions of width direction | Few deep depressions of width direction | Few very deep depressions of width direction |
| Apperance of slab surface on narrow face of slab | Shallow oscillation mark | Shallow oscillation mark (near the top of slab)<br>No oscillation mark due to lack of lubrication (near the tail of slab) | Shallow oscillation mark<br>Better lubrication than NEW5 |
| Change of mold powder composition | Stable.<br>$Al_2O_3$ pick up: <5% | Stable<br>$Al_2O_3$ pick up: <5% | Unstable<br>$Al_2O_3$ pick up: <15% |
| Evaluation | Acceptable for 1.5% TRIP steel casting | Unacceptable due to lack of lubrication | Unacceptable due to unstable mold heat transfer |

## 4. Conclusions

Overall eight cast trials have been carried out for high aluminum TRIP steel using conventional lime-silica and newly develop lime-alumina base mold fluxes at the pilot caster in POSCO. It was shown that the application of the lime-alumina mold fluxes could suppress the occurrence of surface depressions and cracks by stabilizing the mold heat transfer at the initial stage of casting. However, the slag film of lime-alumina mold fluxes were prone to crystallize easily during casting, which made the mold lubrication deteriorate rapidly. Both the castability and surface quality of high aluminum TRIP steel were drastically improved by optimizing the slag chemistry of lime-alumina mold fluxes with the additions of $B_2O_3$, $Na_2O$, $Li_2O$ and controlling the lime to alumina ratio. Future work will focus on further improvement of the lime-alumina base mold fluxes by controlling the crystallinity of the slag film.

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