1. Introduction

Magnesium injection has been proven to be one of the most efficient, economical, fast and environmental friendly processes for hot metal desulfurization in integrated steel-making plant. However, the effect of carrier gas on the magnesium efficiency in the magnesium injection processes is still remained as a puzzling issue in open publications. Some investigations suggested that the magnesium efficiency is lowered by using nitrogen as carrier gas, while many others suggested the effect of nitrogen is small. There was no significant difference in magnesium efficiency can be confirmed between the process using nitrogen and that using argon in experimental or industrial trials. In this study, thermodynamic and kinetic analysis of nitrogenization in magnesium desulfurization process was analyzed. Although magnesium nitride is unstable in the high temperature system formed in magnesium injection process, the nitride is possible to generate at localized regions close to the lance tip. The nitride formed at lance tip may cause lance clogging. Magnesium nitride is unstable in hot metal or in gas at high temperatures; and after leaving lance tip regions, magnesium nitride will undergo decomposition. Magnesium loss in process off gas will be increased by the decomposition of magnesium nitride that occurs too closely to bath surface or by any un-decomposed magnesium nitride at bath surface. The magnesium loss by nitrogenization and the clogging problem could be minimized by optimizing injection conditions.

2. Literature Study

The nitrogenization of solid, liquid or gaseous magnesium may occur during magnesium injection process. These reactions not only consume magnesium but also cause lance clogging problem during magnesium desulfurization process. A statistic analysis of operational data by Chen et al. shows that, there was about 16 to 20% of magnesium is nitrogenized, which heavily reduces the magnesium desulfurization efficiency of the injection process. The nitrogenization loss could be avoided if nitrogen is replaced by argon as carrier gas for the injection. By carefully assessing both aspects of magnesium desulfurization efficiency and carrier gas cost, they selected nitrogen for the injection process.

The performances of the magnesium injection process of a Chinese steelmaker using nitrogen and that of an Ukrainian steelmaker using argon as carrier gas for introducing magnesium granules into hot metal are compared in Table 1. In the injection process using argon gas, magnesium consumed for removing sulfur in hot metal is 1.22 kg Mg/kg S, which is 3% less than that in the process using nitrogen gas where 1.26 kg Mg/kg S was consumed. It is not clear that the slight higher magnesium efficiency in the process using argon is contributed by carrier gas or not.
This is because many process parameters in Ukrainian steelmaker are better than those in Chinese steelmaker for achieving higher magnesium efficiency. For example, the injection is deeper, the size of ladle or the mass of hot metal is larger and the temperature is lower in Ukrainian steelmaker than those in Chinese steelmaker. Therefore, the effect of replacing argon with nitrogen as carrier gas on the magnesium desulfurization efficiency may not be significant.

In the earlier study by Voronova et al., factors that influencing the magnesium desulfurization efficiency were systematically investigated. When compared with nitrogen or air, the higher magnesium desulfurization efficiency was achieved when natural gas was used as carrier gas. According to this result, natural gas is suggested by Sun et al. for improving magnesium desulfurization efficiency of the injection process because magnesium loss by nitrogenization as well as by oxidation will be prevented by natural gas. Furthermore, the carbon and hydrogen decomposed from natural gas at high temperatures will facilitate further desulfurization.

Base on thermodynamic analysis, Li suggested that the nitrogenization of magnesium under nitrogen atmosphere is possible at temperature between 573–1713 K. The magnesium nitride is unstable in air; it will react with moisture in air to produce MgO and NH₃.

To investigate the effect of carrier gas, Nakanishi et al. carried out lab scale experiments where 15 kg blast furnace hot metal was injected by magnesium granulates using argon and nitrogen at 1450°C. The experimental results are shown in Table 2 and the changes of sulfur during the experiments are shown in Fig. 1. In Table 2, the Mg/metal ratio is the amount of magnesium in gram per kg of hot metal. The desulfurization ratio is the fraction of sulfur removed by the magnesium injection, and the Mg utilization ratio is the fraction of injected magnesium that reacted with sulfur in hot metal. As seen in Fig. 1, the desulfurization rate was essentially same in two runs of different carrier gases. This indicates the desulfurization performance is not affected by replacing argon with nitrogen. The desulfurization ratio and the Mg utilization ratio are compared in Table 2 for 2 runs. This comparison clearly shows the similar desulfurization performance in the run with nitrogen and that with argon. Therefore, the effect of nitrogenization on the magnesium desulfurization efficiency is considered unimportant when temperature is as high as 1450°C or when the injection is shallow. According to the visual observation by authors, lance clogging was confirmed when nitrogen was used as carrier gas for injecting magnesium. The lance clogging materials was confirmed to be mixture of Mg₃N₂, MgO and Mg by X-ray diffraction analysis. The clogging phenomenon should bring our attention when nitrogen is used as carrier gas in the practice.

The experimental results shown in Table 2 and Fig. 1 is supported by the thermodynamic analysis by Sun et al. Magnesium nitride (Mg₃N₂) is found to be unstable in hot metal at higher temperatures and therefore the effect of nitrogen as carrier gas is suggested to be insignificant because Mg₃N₂ (if generated) will eventually decompose in the hot metal and Mg(g) generated from the decomposition will contribute to desulfurization.
vere magnesium loss by nitrogenization in the process when nitrogen is used as carrier gas for injecting magnesium granules, while many others suggested the loss is unimportant. No experimental or industrial trial evidence can be found to show the magnesium desulfurization efficiency is deteriorated by nitrogen as compared with argon under otherwise similar injecting conditions. The issue is unfortunately a controversial one in open publications and is needed to be clarified.

3. Thermodynamic and Kinetic Analysis

3.1. Nitrogenization of Magnesium in Injection Process

Figure 2 shows the schematic diagram of hot metal desulfurization process by magnesium injection. Hot metal contained in a ladle is injected with gas–solid mixture through an immersed lance. Magnesium granules are carried by nitrogen gas and injected deeply into metal bath. Magnesium granules are heated up in the lance where a portion of magnesium granules may melt, vaporize or be nitrogenized. The gas forms numerous bubbles after leaving the lance tip. These bubbles rise in hot metal to bath surface. Some of magnesium granules penetrate into hot metal. Immediately after the penetration, magnesium granules rapidly transfer into liquid or magnesium gas bubbles in hot metal at the vicinity of the lance tip where they are consumed rapidly by dissolution into the hot metal.8,9)

The locations of magnesium nitrogenization during magnesium injection process are shown in Fig. 2. These include the nitrogenization of solid and liquid magnesium within the lance, of gaseous magnesium within lance or bubbles, of dissolved magnesium in the vicinity of lance tip, and of magnesium oxide or magnesium sulfide in the active zone.

3.2. Nitrogenization of Solid Magnesium

The magnesium granules carried by nitrogen gas are heated up while they travel in the lance. The solid magnesium may react with nitrogen in the lance through reaction (1).

$$3\text{Mg}(s) + N_2 \rightarrow Mg_3N_2(s)$$ ..........................(1)

$$\Delta G^\circ = -460200 + 202.9T \text{ J/mol (298–922 K) }^{10}$$

Nitrogen pressure in equilibrium with solid magnesium according to reaction (1) is calculated in Table 4. When the nitrogen pressure is larger than the equilibrium nitrogen pressure, reaction (1) occurs to produce Mg$_3$N$_2$. When the nitrogen pressure is below the equilibrium nitrogen pressure, reverse reaction (1) occurs to decompose Mg$_3$N$_2$. The equilibrium nitrogen pressure increases with increasing temperature to the magnesium melting temperature of 922 K where the nitrogen pressure reaches maximum of $3.4 \times 10^{-16}$ atm. The gas pressure in the lance is well above 1 atm and nitrogen is close to 100% in the gas. Therefore, thermodynamically, it is possible for Mg(s) to react with N$_2$ to produce Mg$_3$N$_2$ during magnesium granules traveling in the lance. However, from the kinetic point of view, the reaction (1) is unlikely to occur. This is because the residence time of magnesium granules in the lance, which is estimated to be less than 0.13 second for an injection process with lance ID of 0.02 m, gas flowrate of 100 m$^3$/h and injection depth of 3.5 m, is too short for a noticeable reaction. Furthermore, the surface of magnesium granules is usually coated with inactive salt materials which will prevent solid magnesium from directly exposing to nitrogen and being nitrogenized in the lance.

3.3. Nitrogenization of Liquid Magnesium

If a portion of magnesium granules melts in lance, the liquid magnesium will react with nitrogen by reaction (2).

$$3\text{Mg}(l) + N_2 \rightarrow Mg_3N_2(s)$$ ..........................(2)

$$\Delta G^\circ = -489440 + 232.6T \text{ J/mol (922–1362 K) }^{10}$$

Nitrogen pressure in equilibrium with liquid magnesium according to reaction (2) is also given in Table 4. Similarly, when the nitrogen pressure is above the equilibrium pressure, reaction (2) will occur to produce Mg$_3$N$_2$. Thermodynamically, it is possible for Mg(l) to react with N$_2$ to produce Mg$_3$N$_2$ in the lance since the equilibrium pressure varies between $2.6 \times 10^{-11}$ atm at 922 K to $2.4 \times 10^{-7}$ atm at 1362 K which is far below nitrogen pressure in the lance. However, for a lance without an evaporator, the reaction (2) may not occur properly since the residence time of magnesium granules in the lance may be too short for melting magnesium. Even magnesium granules has a chance to melt in the lance, the time of liquid magnesium exposure to nitrogen gas in the lance would be very limited for reaction (2).
3.4. Nitrogenization of Gaseous Magnesium

When magnesium vaporizes into magnesium gas in lance or in an evaporator if it is used at lance tip, magnesium vapor will join to the gas to form a gas of N$_2$–Mg(g) mixture. The gas then forms numerals gas bubbles in hot metal after leaving the lance tip. The bubbles may absorb more magnesium vapour from hot metal in the vicinity of the lance tip since magnesium content in the hot metal close to the lance tip could be much higher. For the N$_2$–Mg(g) mixture within the lance, evaporator or gas bubbles, the reaction (3) will occur.

$$3\text{Mg}(g) + \text{N}_2 = \text{Mg}_3\text{N}_2(s)$$

$$\Delta G^\circ = -868\ 200 + 510.8 T\text{ J/mol (1 362–1 700 K)}^{(10)}$$

If the total gas pressure is known and there is no gaseous species other than magnesium vapor and nitrogen in the system, the equilibrium gas composition can be calculated at a given temperature and under total pressure of $P_t = P_{\text{Mg}} + P_N$. Figure 3 and Table 4 shows the partial pressures of magnesium and nitrogen, and magnesium content in the gas of N$_2$–Mg(g) binary system in equilibrium with Mg$_3$N$_2$(s) at 1 350°C as a function of total gas pressure. The partial pressure and content of magnesium decrease, and the partial pressure of nitrogen increases, with increasing the total pressure. When magnesium vapor pressure or content is above the lines in Fig. 3, reaction (3) will occur to produce Mg$_3$N$_2$. This suggests that Mg$_3$N$_2$ is more likely to be produced by reaction (3) at higher pressure or when the gas bubbles present deeper in the hot metal. In Table 4, the gas pressure ($P_t = 3.37\text{ atm}$) is the hydrostatic pressure at 3.5 m deep in hot metal.

The influence of temperature on the equilibrium Mg(g) content in gas under given total pressures is shown in Fig. 4. The Mg(g) content increases exponentially with increasing temperature especially under lower total gas pressure. This indicates the Mg loss or lance clogging by nitrogenization could be severe if the temperature is too low. For example, under 4 atm and at 1 200°C, Mg$_3$N$_2$ will be produced if Mg(g)$>0.68\text{ vol\%}$ in the gas bubble but Mg$_3$N$_2$ will not be produced if Mg(g)$<11.9\text{ vol\%}$ at 1 400°C under same pressure.

Kinetically, when Mg(g) in gas is above the dashed line in Fig. 3, the reaction (3) will occur rapidly because it is a homogeneous reaction between two gas components in the mixture. The equilibrium of reaction (3) is considered to be established in lance tip or in the gas bubbles if Mg$_3$N$_2$ is present.

3.5. Nitrogenization of Dissolved Magnesium

Once magnesium granules penetrate into hot metal at the lance tip, the granules is rapidly vaporized and this is followed by the dissolution into the hot metal in front of the lance tip. Meanwhile, numerous gas bubbles are generated by the nitrogen carrier gas at the lance tip. At the bubble surface, following reaction occurs between dissolved magnesium and nitrogen gas.

$$3[\text{Mg}] + \text{N}_2 = \text{Mg}_3\text{N}_2(s)$$

The equilibrium constant for reaction (4) can be derived from Gibbs free energy change for reaction (3) and the equilibrium constant for magnesium dissolution reaction (Mg(g)=[Mg], $\ln K = 7\ 000/T - 5.1^{(11)}$). The equilibrium [Mg] content in a typical hot metal containing (mass%) 4.5 carbon, 0.5 silicon, 0.2 manganese, and 0.1 phosphorus is obtained from equilibrium constant of reaction (4) and interaction parameters.$^{12,13}$

The influences of temperature and gas pressure on the equilibrium [Mg] content in hot metal are shown in Fig. 5. The equilibrium [Mg] content in hot metal increases with increasing temperature. This indicates that the formation of magnesium nitride by reaction (4) is unlikely at higher temperatures. The equilibrium [Mg] is reduced if gas phase is pressurized, and hence the formation of magnesium nitride is favored at high pressure. For example, if the injection
depth is 3.5 m, the gas pressure is 3.37 atm, it can only tolerate 0.1 mass% [Mg] in the hot metal without formation of magnesium nitride at 1350°C. In the other words, magnesium nitride will be generated by reaction (4) at the lance tip region when magnesium content in hot metal is higher than 0.1 mass%. This is an unfortunate situation since the magnesium content will be kept very high in the hot metal at the vicinity of the lance tip by the continuous supply of magnesium granules from the lance. High [Mg] and high $P_{\text{N}_2}$ at lance tip region form a system of excellent thermodynamic conditions for magnesium nitrogenization, and this unfortunate situation will become even worse at lower temperatures. The nitride formed at lance tip region is believed to be responsible for the lance clogging problem that would seriously damage smooth injecting.

### 3.6. Nitrogenization of Magnesium Sulfide

The nitrogen gas bubbles may react with the desulfurization product, MgS, to produce magnesium nitride by the reverse reaction (5). Kinetically, the reverse reaction (5) in a magnesium injection process is not easy since it requires the contact between the solid MgS particles and nitrogen bubbles in hot metal bath. Both gas bubbles and MgS particles are dispersed phases in hot metal and they have little chance to meet one another in the bath. Instead, if there is magnesium nitride in the hot metal, the magnesium nitride would be decomposed by reaction (5).

$$3[S] + Mg_3N_2(s) = 3MgS + N_2 \quad \Delta G^0 = -345840 - 1947T \ \text{J/mol}^{[9]}$$

Decrease in temperature or in nitrogen pressure will bring the equilibrium sulfur content lower in hot metal, which will facilitate reaction (5) to decompose magnesium nitride. In fact, this reaction is welcome because it not only prevents magnesium loss as nitride but also contributes to desulfurization of hot metal. [S] content in the typical hot metal in equilibrium with magnesium nitride at 1350°C given in Table 4 is obtained by equilibrium constant of reaction (5) and interaction parameters, and it is well below 1 ppm. If there is any magnesium nitride present in hot metal, it will decompose through reaction (5) since hot metal usually contains much higher sulfur content.

### 3.7. Nitrogenization of Magnesium Oxide

Some magnesium is oxidized by oxygen in hot metal to produce magnesium oxide, which may in turn react with nitrogen bubbles through reverse reaction (6). Similar as discussed with reverse reaction (5), the reverse reaction (6) is kinetically unlikely to occur. On the other hand, magnesium nitride would decompose by the reaction with oxygen in the hot metal through reaction (6).

$$3[O] + Mg_3N_2(s) = 3MgO + N_2 \quad \Delta G^0 = -978450 + 115.9T \ \text{J/mol}^{[10]}$$

The equilibrium oxygen content in a typical hot metal at 1350°C is obtained by the equilibrium constant of reaction (6) and interaction parameters, and the equilibrium oxygen is found extremely low in the hot metal as seen in Table 4. This indicates the magnesium nitride is unstable in hot metal and tends to decompose through reaction (6). The equilibrium oxygen content in hot metal is further reduced and thus $Mg_3N_2$ is more unstable at lower temperature or lower nitrogen pressure. The equilibrium oxygen content is much lower than oxygen content observed in industrial practice, and therefore, magnesium nitride present in hot metal will undergo decomposition by oxygen in hot metal through reaction (6).

![Fig. 6. Thermodynamic and kinetic analysis of nitrogenization reactions in magnesium injection process.](image)

### 4. Magnesium Loss by Nitrogenization

The thermodynamic and brief kinetic analysis of nitrogenization reactions in magnesium injection process in Sec. 3 is summarized in Fig. 6. The magnesium nitride is most likely to be produced by reactions (3) and (4) within or outside of lance tip. The question is whether magnesium nitride generated at the lance tip region is responsible for magnesium loss in magnesium injection process or not. To answer this question, the behavior of magnesium nitride in the process is worth to be further explored.

### 4.1. Magnesium Nitride in Hot Metal

As schematically shown in Fig. 7(a), if magnesium nitride produced at lance tip has a chance to leave the lance tip region and rise in the hot metal, the magnesium nitride will easily undergo decomposition reaction through reverse reaction (3), and reaction (5) or (6), therefore the magnesium loss as nitride may be avoided.

### 4.2. Magnesium Nitride at Lance Tip

It will be problematic if magnesium nitride is generated at the lance tip and is attached to the inner or exterior wall of the lance as schematically shown in Fig. 7(b). This is be-
cause the thermodynamic conditions in the vicinity of lance tip (high [Mg] and high $P_{N_2}$) will not allow magnesium nitride to decompose. The nitride attached to the lance tip will cause nozzle clogging or even nozzle blocking. The clogged materials at lance tip were confirmed by Nakanishi and co-workers\(^6\) as the mixture of Mg$_3$N$_2$, MgO and Mg. It was found that the amount of clogged materials is small and the effect of magnesium nitride attached at lance tip on the magnesium efficiency is considered unimportant. The clogged magnesium nitride at lance may be eliminated by post blowing of nitrogen in practice.

4.3. Magnesium Nitride in Gas Bubbles

Magnesium nitride may present in gas bubble as suspended particles in gas as schematically shown in Fig. 7(c). The magnesium nitride could enter gas bubbles at lance tip region through four different routes. Firstly, magnesium nitride may be generated by the nitrogenization of solid, liquid and gaseous magnesium through reactions (1)–(3) while magnesium granules traveling with nitrogen in the lance or in an evaporator where some granules may partially/fully melt or vaporize. Secondly, the direct nitrogenization of dissolved magnesium through reaction (4) at gas–hot metal interface in front of lance tip may produce magnesium nitride in gas phase. Thirdly, the indirect nitrogenization of the dissolved magnesium may occur through two separate steps in series; the first step is the vaporization of dissolved magnesium into nitrogen bubble, which is followed by the second step of the nitrogenization of the vapor by reaction (3) within the bubble. Finally, magnesium nitride generated at the lance tip may enter hot metal and undergo decomposition through reverse reactions (3)–(6); the decomposition would directly form gas bubbles which may contain some un-decomposed magnesium nitride particles.

Depressurization of bubbles and decrease of Mg(g) content in gas phase by the reaction between bubble and hot metal during the bubble rising in hot metal will trigger co-cooned nitride particles to decompose through reverse reaction (3). The decomposition of magnesium nitride within bubbles is important for bubble-hot metal reaction since Mg(g) content in bubble will be maintained higher as the bubble rises. Mg(g) content in bubble at the bath surface could be high which leads to heavy magnesium vapor loss to atmosphere. Furthermore, any un-decomposed magnesium nitride in the bubbles at bath surface will also be lost to atmosphere. These aspects should be confirmed in future.

4.4. Minimization of Mg Loss by Nitrogenization

There are several methods that could be attempted to minimize nitrogenization. For example, to increase bath agitation to reduce local [Mg] content in lance tip regions, to increase gas/solid ratio to reduce Mg(g) content in gas, to shorten residence time of magnesium granules in the lance, to use direct injection lance without an ante-chamber (evaporator) at lance tip, to increase temperature of hot metal, to decrease pressure, and to apply post nitrogen blowing. However, the choice of these methods should be balanced by their influences on the other reactions in the process, and a careful optimization is needed.

5. Conclusions

Literature study shows that the magnesium efficiency for magnesium desulfurization processes may be deteriorated by using nitrogen as carrier gas, but the difference in magnesium efficiency for the processes using argon and nitrogen is not confirmed in practice. Thermodynamic and kinetic analysis shows that Mg$_3$N$_2$ is unstable in hot metal at high temperatures or low pressures. It is possible for Mg$_3$N$_2$ to generate in the regions close to the lance tip and to cause lance clogging problem. Any Mg$_3$N$_2$ leaving lance tip region will either enter hot metal or be cocooned in gas bubbles where Mg$_3$N$_2$ undergoes decomposition. The magnesium loss for an injection process will be increased by the un-decomposed Mg$_3$N$_2$ at bath surface or by the decomposition reaction that occurs closely to the bath surface. The magnesium loss by nitrogenization and the clogging problem could be minimized by optimizing injection conditions such as bath agitation, gas/solid ratio, injecting speed, lance design, temperature, pressure and post nitrogen blowing.

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