Improvement of Alumina-Magnesia Castables for Ladle and its Corrosion Mechanism

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The main purpose of this study is to improve the properties of alumina-magnesia castables and explore its corrosion mechanism. (1) Using different additives to improve the flowability, the dispersive effect from best to worst is polymer dispersant A, polymer dispersant B, sodium hexametaphosphate and sodium tripolyphosphate. However, sodium hexametaphosphate is easier to deliquescence, and polymer dispersant B contains a small amount of Na, which reduces the melting point of the alumina-magnesia castables and affects the refractoriness. Therefore, it is recommended that polymer dispersant A as the main dispersant. (2) In terms of the improvement of explosion resistance, this study tested different ratios of magnesia, aluminum, silica and fiber. The results revealed that the most critical factors affecting the explosion resistance are fiber and aluminum powder. After comprehensive performance considerations, the most suitable additions are magnesia (A%), aluminum (B%), silica (C%), and fiber (D%). In addition, the residual lining of the alumina-magnesia castables was sampled for microstructure analysis. It showed that the molten steel/slag reacted with the alumina-magnesia castables to form the phases with low melting point such as CA($CaAlO_4$) and $C_{12}A_7$($CaAl_{12}O_7$), which adhered to the surface of the castables and penetrated it. It was also observed that the matrix area of the alumina-magnesia castables was corroded first and then the aggregate area was exposed, which would result in the spalling phenomena. If the life time of alumina-magnesia castables needs to be increased in the future, the improvement of the matrix can be carried out first, followed by the improvement of the aggregate.

Keywords: Ladle, Alumina-magnesia castables, Dispersant, Explosion resistance

1. INTRODUCTION

In recent years, the production technology of clean steel has developed rapidly, so the secondary refining of steel in the ladle has become more important. However, the diversification of steel grades and the increase in steel casting temperature has led to harsher operating conditions for the ladles. Therefore, the refractory material of the working lining in a ladle must have the following characteristics: (1) excellent explosion resistance, (2) highly resistant to iron oxide corrosion, (3) high resistance to steel penetration, (4) thermal shock stability, (5) high strength, (6) better resistance to steel erosion, etc. The refractory material of the working lining in a ladle is alumina-magnesia castables, which is mainly composed of Al_2O_3 and MgO. In general, its aggregate is made of fused corundum, brown corundum and tabular corundum. The fine powder part contains alumina, calcium aluminate cement, silica, fiber and various additives. Common problems of alumina-magnesia castables in steel ladles are as follows: (1) The poor flowability leads to high porosity after castable casting, which will reduce the life time of the steel ladle, (2) The explosion during the preheating process makes for the refractory materials having to be reworked, resulting in scheduling difficulties and rising steelmaking costs. If the crack is in the form of a micro-crack and is hard to be detected visually, it will cause the molten steel to penetrate the ladle and lead to industrial accidents such as steel leakage. In terms of castable flowability, it can be improved by introducing different types of dispersants. Furthermore, the explosion resistance can be enhanced by different kinds of anti-explosion additives as follows: (1) The addition of aluminum powder can significantly improve the explosion resistance of refractories. Aluminum powders with different particle sizes have different explosion resistances. Aluminum powders with ≤0.15 mm have better performance than those with ≤0.075 mm and ≤0.25 mm, which means aluminum powders have to exist with suitable particle size to be effective to explosion resistance[1-3]. (2) Adding an appropriate amount of azodimethylamine can prevent the castables of iron runner from explosion under the preheating condition of 500~800°C. However, the increase of azodicarbonamide caused a large number of cracks inside the castables reducing its strength(4). (3) The length and amount of anti-explosion fiber (polypropylene fiber) have a significant effect on the permeability, porosity, explosion resistance and strength of the castables. It is mentioned that fibers with a length of ≧ 3mm can significantly increase the permeability of the castables and the fiber addition with 0.06% has the best performance(5-7). (4) Compound addition of anti-explosion additives (aluminum powder and fiber) can optimize the performance of castables. The key is to control the particle size of the aluminum powder, the fiber type and additional quantity(8-12). In this work, the main purpose is to improve the flowability of alumina-magnesia castables and enhance its explosion resistance. In addition, the residual refractories after use were sampled to explore the corrosion mechanism.

2. EXPERIMENTAL METHOD

The composition of alumina-magnesia castables for steel ladles is divided into three types, including aggregates (particle size >200mesh), powders (particle size ≤200mesh) and special additives. In this study, the aggregates selected were fused corundum with a purity of ≥99%, and particle sizes of 5~8mm, 3~5mm, 1~3mm and 0.075mm~1mm. Powders use alumina (α-Al_2O_3 ≥99%, D50≤5um), magnesia (MgO ≥90%, particle size ≤200mesh) and silica (SiO_2 ≥97%, particle size ≤1um). In terms of special additives, calcium aluminate cement (Al_2O_3 ≥70wt%, CaO ≤30wt%) is used as the binder, and the sodium hexametaphosphate, sodium tripolyphosphate, polymer type dispersant A and dispersant B will be tested as dispersants. Anti-explosion additives are selected from aluminum powder (purity ≥95%, particle size ≤200mesh) and polyvinyl alcohol (PVA) fiber with a diameter of 3mm. This study is mainly divided into 3 Phases. Phase-(1) is the selection of different dispersants to improve the flowability of alumina-magnesia castables; Phase-(2) is to improve the explosion resistance. The experimental design by using Minitab software is shown in Table 1. The experimental factors and levels are magnesia (A-1%, A%, A+1%), aluminum (B%, 2B%, 3B%), silicon dioxide (C-0.03%, C%, C+0.03%) and fiber (D-0.03%, D%, D+0.03%); Phase-(3) is the analysis of residual lining and the corrosion mechanism of alumina-magnesia castables. In terms of sample preparation, the alumina-magnesia castables were firstly prepared with aggregates, powders and additives in proportions. To add an appropriate amount of water to the mixer, mix for 3 minutes, pour it into the mold and let it stand for 24hrs. After de-molding, the samples are dried in an oven at 110°C/24hrs, and then sintered at 1500°C /3hr for property analysis. The analysis items include as follows: (1) The standard test method for measuring consistency of self-flowing castable refractories (ASTM C1446-19); (2) The density tester (Precondar, XQK-04) for bulk density (BD) and apparent porosity (AP); (3) Refer to JIS R2208 for permanent linear change (PLC) measurement; (4) The universal testing machine (Hung-Ta, HT-2402) for modulus of rupture (MOR) by ASTM C583-15; (5) The strength tester for cold crushing strength (CCS) at room temperature by ASTM C133-97; (6) Refer to GB/T36134 to measure the explosion resistance. The experimental steps are that the sample after mixing with water was poured into the mold and left for 24 hours, and then placed in a furnace at 1000°C/15min to observe the explosion behavior; (7) The steel block test selects medium carbon steel and the test temperature was 1600°C/15min for the penetration test of molten steel (JIS R2214); (8) Microstructural analysis and corrosion mechanism study by using polarized light microscopy and scanning electron microscopy (SEM/EDS).

Table 1 DOE experiment for improving explosion resistance of alumina-magnesia castables

Sample	Magnesia	Aluminum	Silica	Fiber
AM-1	A-1%	B%	C-0.03%	D-0.03%
AM-2	A-1%	2B%	C%	D%
AM-3	A-1%	3B%	C+0.03%	D+0.03%
AM-4	A%	B%	C%	D+0.03%
AM-5	A%	2B%	C+0.03%	D-0.03%
AM-6	A%	3B%	C-0.03%	D%
AM-7	A+1%	B%	C+0.03%	D%
AM-8	A+1%	2B%	C-0.03%	D+0.03%
AM-9	A+1%	3B%	C%	D-0.03%

3. RESULTS AND DISCUSSION

3.1 Flowability Improvement with Different Dispersants

Cement or fine powder dispersed in water is a thermodynamically unstable system easily leading to flocculation[13~16]. The reasons for the formation of flocculation structure are as follows: (1) The mineral phases of cement are attracted by different charges after hydration; (2) Fine particles attract each other during collision in water; (3) Van der Waals forces between fine particles. Therefore, the main function of the dispersant is to destroy the flocculation structure to release the coated water and disperse the particles to achieve the purpose of water reduction and dispersion. In general, the choice of dispersant has a significant impact on the effects of cement-based castables. The traditional dispersants of alumina-magnesia castables are phosphates, such as sodium tripolyphosphate and sodium hexametaphosphate. However, phosphate-based dispersants have poor water-reducing effect and are susceptible to moisture and difficult to store. In this study, the different brands of polymer dispersant A and polymer dispersant B are introduced for test. Both of these are polymer-based dispersant of Polycarboxylate ethers (PCEs). Its molecular surface has a "charged backbone" that can change the surface charge of the powder to generate electrical repulsion. It also has "side chains" to block powder flocculation in a physical space. This is the main reason for effectively reducing water and improving flowability.

The experiment is to fix the aggregate/powder ratio of the alumina-magnesia castables and test the effect of different dispersants (Sodium tripolyphosphate, sodium hexametaphosphate, polymer type dispersant A and B) on the flowability and physical properties at the same addition of 0.1wt%. The results are shown in Table 2 and Table 3. It shows that the effect of different dispersants on the flowability of castables is from best to worst: polymer type dispersant A, dispersant B, sodium hexametaphosphate, sodium tripolyphosphate. However, sodium hexametaphosphate is easy to deliquescence, and the polymer dispersant B contains a small amount of Na, which would reduce the melting point of the alumina-magnesia castables and affect the refractoriness. Therefore, it is recommended that the polymer dispersant A as the main dispersant. The analytical items of the influence of dispersant on the physical properties include bulk density (BD), apparent porosity (AP), cold crushing strength (CCS), modulus of rupture (MOR) and permanent linear change (PLC). The results show that the use of different dispersants has no obvious effect on the physical properties of the castables.

3.2 Enhancement of Explosion Resistance

Compound addition of anti-explosion additives (aluminum powder and fiber) can optimize the performance of castables. The key is to control the particle size of aluminum powder, the fiber type and additional quantity[8-12]. Phase-(2) is to fix the ratio of aggregate/powder and design Taguchi L9-DOE experiment by Minitab software to find out the optimum ratio of magnesia powder, aluminum powder, silica powder and fiber addition to the explosion resistance of castables. The experimental design is shown in Table 1. In terms of the effect on flowability, the experimental data and the calculation results of Minitab are shown in Table 4 and Figure 1, respectively. The results show that the factors affecting the flowability at a fixed water addition are fiber, silicon

Table 2 Effects of different dispersants on the flowability of alumina-magnesia castables

Sample	Dispersant	Water amount (wt%)	Flowability (%)
AM-(a)	Dispersant A	6.0	100
AM-(b)	Dispersant B	6.0	95
AM-(c)	Sodium tripolyphosphate	6.0	55
AM-(d)	Hexametaphosphate	6.0	68

Table 3 Effects of different dispersants on the physical properties of alumina-magnesia castables

Sample	Dispersant	PLC (%)	MOR (MPa)	CCS (MPa)	AP (%)	BD (g/cm3)
AM-(a)	Dispersant A	+1.59	23.1	76.9	23.9	2.88
AM-(b)	Dispersant B	+1.61	21.7	67.2	24.5	2.87
AM-(c)	Sodium tripolyphosphate	+1.52	25.1	73.5	23.8	2.88
AM-(d)	Hexametaphosphate	+1.51	22.4	65.5	22.9	2.91

oxide, aluminum, and magnesia in order from high to low. In addition, the Minitab software also calculates the flowability prediction equation.

Flowability (unit: mm) = 170 + 2.17*Magnesia+ 80*Aluminum - 38.3*Silica - 433*Fiber

The results of the effect on physical properties are shown in Table 5. The samples AM-2 and AM-4 performed the best in various physical properties.

Table 4 Water addition and flowability of alumina-magnesia castables in anti-explosion experiments

Sample	Water addition (wt%)	Flowability (%)
AM-1	6.0	134
AM-2	6.0	120
AM-3	6.0	103
AM-4	6.0	96
AM-5	6.0	102
AM-6	6.0	131
AM-7	6.0	121
AM-8	6.0	111
AM-9	6.0	132

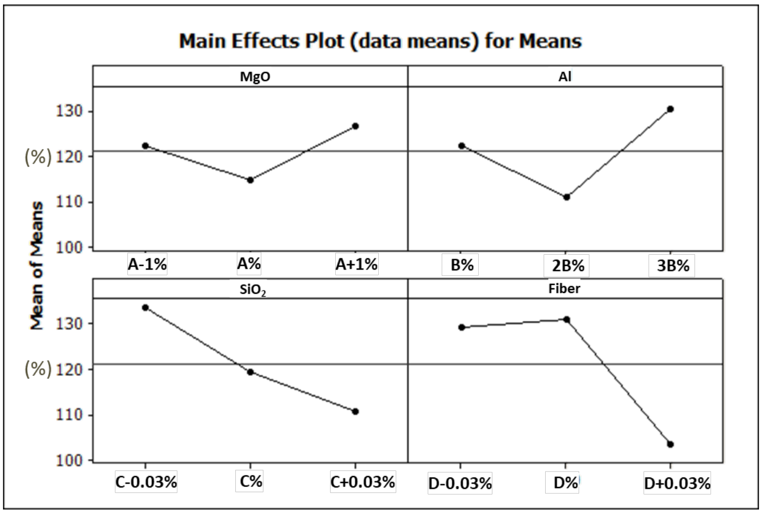


Fig.1. Minitab software analysis results of flowability in anti-explosion experiments

Table 5 Physical properties of alumina-magnesia castables in anti-explosion experiments

Sample	Physical properties (@1500℃/3hr)				
	PLC (%)	MOR (MPa)	CCS (MPa)	AP (%)	BD (g/cm^3)
AM-1	3.03	15.78	50.30	26.13	2.80
AM-2	1.40	20.93	72.07	22.83	2.89
AM-3	0.40	20.45	95.04	21.47	2.95
AM-4	1.46	18.60	65.39	24.56	2.85
AM-5	0.41	22.19	89.73	21.06	2.96
AM-6	2.76	13.10	45.59	26.58	2.80
AM-7	0.58	21.66	78.70	22.16	2.92
AM-8	2.67	13.44	49.29	23.98	2.79
AM-9	1.78	17.36	70.62	23.74	2.87

ANOVA main effect analysis and regression prediction curve for PLC and MOR by Minitab are shown in Figure 2. Since PLC tends to the target range (+1~+2%), the content of silica should be controlled to C% and the remaining factors are effective less by aluminum, magnesia and fiber.

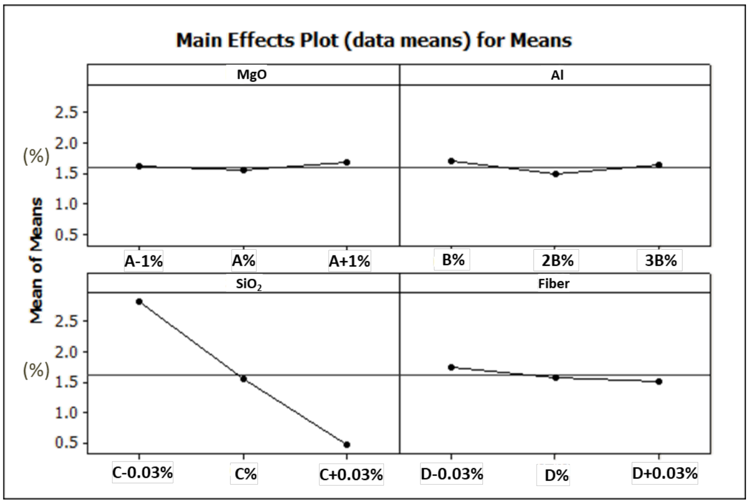
PLC prediction equation (unit:%) = 3.83 + 0.107* Magnesia + 1.43*Aluminum - 3.70*Silica - 3.39* Fiber

The value of MOR tends to be large (≧15 MPa). The main influence on MOR is silica, and the more it is added, the higher the strength of the castables. Followed by aluminum powder, the less the amount, the stronger the strength. However, the PLC considers that the upper limit of Silica is C%, so the recommended amount of aluminum powder has to be B%.

MOR prediction equation (unit: MPa) = 9.06 + 0.068*Magnesia - 35.7*Aluminium + 18.8*Silica + 6.4*Fiber

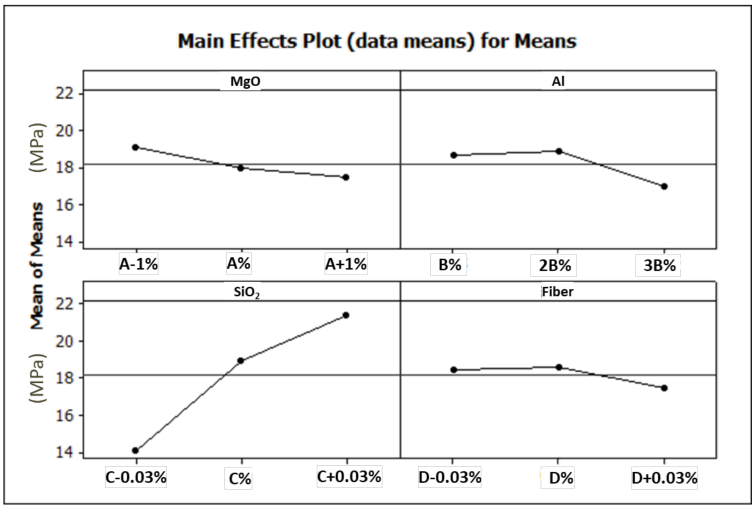
Table 6 is the explosion resistance results of samples AM-1~AM-9. The samples are poured and placed for 24hrs, and then sintered at 1000℃/15min to observe the explosion resistance. It showed that AM-6 performed best, followed by AM-4 and AM-1. The explosive phenomena and surface crack state of the samples were graded, and then analyzed by Minitab software. The results revealed that the most critical factors affecting the explosion resistance are fiber and aluminum powder.

PLC (+1~+2 %，Nominal-The-Best，NTB)



(a)

MOR (≧15 MPa，Larger-The-Better ，LTB)



(b)

Fig.2. Minitab software analysis results of alumina-magnesia castables in anti-explosion experiments (a). For PLC; (b). For MOR

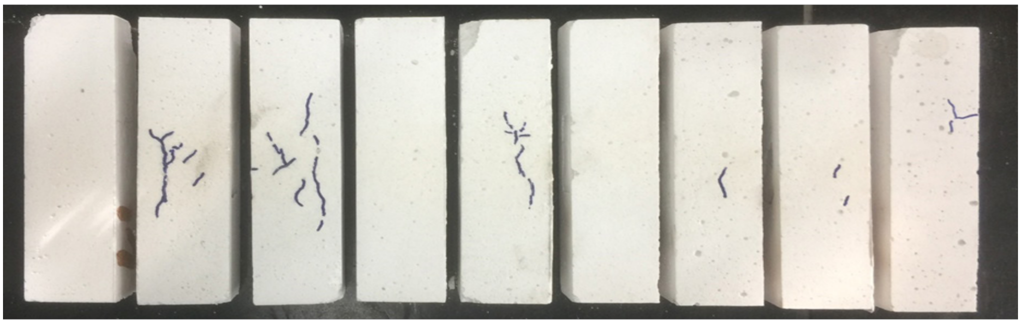
This can be interpreted as that the fiber is an organic substance with a low melting point, which will be burnt out during the preheating process of the ladle and then generate a gas channel inside the castable refractories for water evaporation. In addition, the reaction of aluminum powder and water will generate alumina and hydrogen. The reaction equation of aluminum and water is $2Al+6H_2O=2Al(OH)_3+3H_2$. The process of hydrogen production also creates a gas channel inside the castables for water evaporation. Considering the above flowability, physical properties and explosion resistance, the most suitable additions are magnesia powder (A%), aluminum powder (B%), silica powder (C%), and fiber (D%).

3.3 Analysis of Residual Lining and Corrosion Mechanism

The alumina-magnesia castables are often used in the ladle as the working lining to carry the molten steel and its corrosion mechanism as shown in Figure 3. The refractories first react with the molten steel to form a liquid interface layer, and then the layer will be emulsified and mixed with the molten steel. After that, the molten steel reacts with the new interface of the refractories. The cycle of the above process leads to continuous corrosion and the increase of inclusions in the molten steel [17]. If an interface layer with a high melting point (Ex: magnesia-alumina spinel) formed during the

Table 6 Test results of explosion resistance of alumina-magnesia castables

Sample	Explosion resistance	Score (5→1)
AM-1	No cracks	5
AM-2	Surface microcracks	2
AM-3	Surface microcracks	2
AM-4	No cracks	5
AM-5	Surface microcracks	3
AM-6	No cracks	5
AM-7	Surface microcracks	4
AM-8	Surface microcracks	4
AM-9	Surface microcracks	4



From left to right are AM-1 to AM9

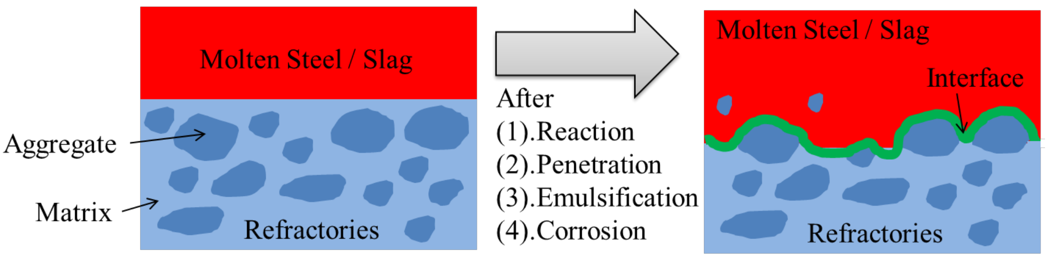


Fig.3. Schematic illustration of corrosion mechanism of ladle working lining.

process, it would retard and inhibit the corrosion behavior to the refractory material. The residual lining of the alumina-magnesia castables after the molten steel penetration test was analyzed by polarized light microscope and electron microscope (SEM/EDS). The experimental results are shown in Figure 4. The mixed state of molten steel and slag first reacted with the alumina-magnesia castables to form the phases with low melting point such as CA($CaAlO_4$) and $C_{12}A_7$($CaAl_{12}O_7$) [18]. These adhered to the exterior of the alumina-magnesia castables to make the surface rougher and penetrate it. The new reaction layer attached to the old one causing the reaction layer to be thickened and then peeled off. The residual thickness of the alumina-magnesia castables were getting thinner as a consequence. In addition, it was observed that the matrix area of alumina-magnesia castables were first corroded by molten steel/slag and then exposed to the aggregate area. When the matrix area was corroded significantly, the aggregate area would spall into the molten steel/slag. Therefore, if the steel plant wants to increase the life of alumina-magnesia castables and the number of ladle operation cycles in the future, the performance improvement of the matrix area can be carried out first, and then the enhancement of the aggregate area.

4. CONCLUSION

The common problems in the use of alumina-magnesia castables on steel ladles in steelmaking plants include poor flowability and ease of explosion during the preheating process. In turn will reduce the life time of the steel ladle, increase the cost of steelmaking and also cause industrial safety accidents such as steel leakage. Therefore, the main purpose of this study is to improve the above problems and explore its corrosion mechanism. (1) Using different additives to improve the flowability of the castables, the order from best to worst is polymer dispersant A, polymer dispersant B, sodium hexametaphosphate and sodium tripolyphosphate. However, sodium hexametaphosphate is easy to deliquescence, and the polymer dispersant B contains a small amount of Na, which reduces the melting point of the alumina-magnesia castables and affects the refractoriness. Therefore, it is recommended that polymer dispersant A as the main dispersant. (2) In terms of the improvement of explosion resistance, this study tested

(a)

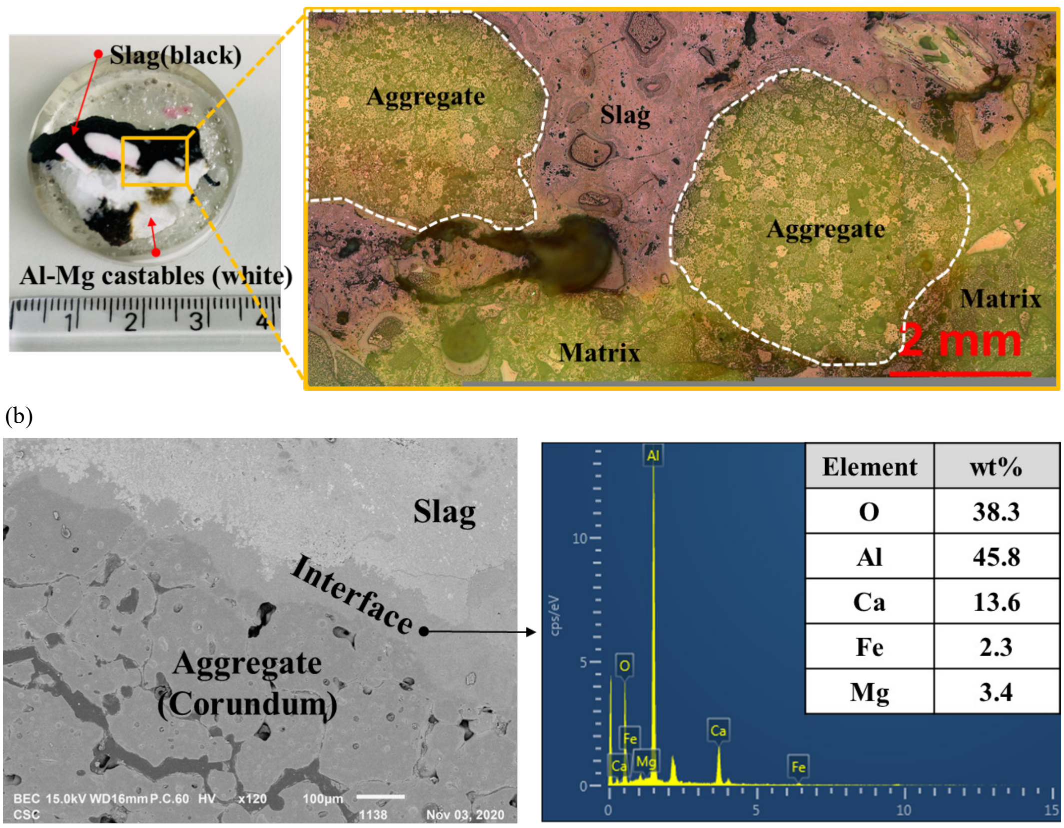


Fig.4. Analysis of residual lining of alumina-magnesia castables: (a) polarized light microscope; (b) electron microscope (SEM/EDS)

different ratios of magnesia, aluminum, silica and fiber. The results revealed that the most critical factors to explosion resistance are fiber and aluminum powder. After comprehensive performance considerations, the most suitable additions are magnesia (A%), aluminum (B%), silica (C%), fiber (D%). In addition, the residual lining of the alumina-magnesia castables was sampled for microstructure analysis. It showed that the molten steel/slag reacted with the alumina-magnesia castables to form the phases with low melting points such as CA($CaAlO_4$) and $C_{12}A_7$($CaAl_{12}O_7$), which adhered to the surface of the castables and penetrated it. It was also observed that the matrix area of the alumina-magnesia castables was corroded first and then the aggregate area was exposed. When the matrix area was corroded significantly, the aggregate area would spall into the molten steel/slag. If the life time of alumina-magnesia castables needs to be increased in the future, the enhancement of the matrix area can be carried out first, followed by the improvement of the aggregate one.

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