Effect of Aluminum and Silicon Antioxidants Addition on Porosity, Cold Crushing Strength, Wear Resistance and Hydration Effect of Alumina Spinel Refractories

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Abstract. Due to their high resistance and wear resistance, alumina spinel (MgAl$_2$O$_4$) are widely used for slide gate on ladle. The characteristics strongly depend on the formation of ceramic phases in the matrix. Addition of antioxidants is used to prevent the graphite oxidation, possibly leading to porosity increase. Currently, other problem appears as the consequences of climate change. The object of this research is to study the effect of antioxidants addition in temperature variations. The influence of Al and Si addition is investigated by means of XRD, SEM, TGA-DTA, apparent porosity, CCS, wear resistance and hydration resistance tests. It was found that lowest porosity, highest CCS and best wear resistance were reached by sample containing Al 5% in 1400°C, while best hydration resistance was reached by sample containing Si 5%.

Keywords: spinel, antioxidant, porosity, CCS, wear resistance, hydration

1. Introduction

The increasing of steels and iron production affects refractories demand generally. In 2016, the usage of refractories for steels and iron industries reached 60% of all refractories demand in the world [1]. Refractories are widely used for slide gate in ladle. Magnesium alumina (MgAl$_2$O$_4$) refractory was applied due to its low thermal expansion, high melting point, stability in chemical environment and good corrosion resistance [2-5]. In advanced research, graphite was added to improve its wear resistance and cold crushing strength. However, graphite was easily oxidized on low temperature that caused the porosity increase and strength decrease. The antioxidants (Al, Si, Mg, C) were added to prevent the graphite oxidation.

Climate change is another problem in refractory industry. According to Indonesian Agency for Meteorology, Climatology and Geophysics (BMKG), Indonesia had its first wet-dry season in 2016 that the rain intensity in summer was higher than usual [6]. The condition would increase vapor and caused refractories disintegration during handling and inventory process.
In this research, the effect of antioxidants addition on refractories properties with variation of temperature was studied. The aim of aluminum addition is to improve the strength and wear resistance, while the silicon addition is to improve the hydration resistance [7]. Several experimental tests were carried out for a better understanding of the antioxidants performance and the characterization of the refractory properties.

2. Materials and Methods

Commercial AR90 alumina spinel with different size aggregate was mixed with tubular alumina, phenolic resin, graphite and variations of antioxidants until homogenized. Antioxidants used were aluminum and silicon metal powder. Antioxidants were added with variations of 5 wt.% Al, 3 wt.% Al + 2 wt.% Si, 2 wt.% Al + 3 wt.% Si and 5 wt.% Si. The mechanical mixing was done twice; dry mixing and resin mixing. After mixing, aging was conducted for 24 hours in room temperature to form resin polymerization. Then, pressing was conducted using Uniaxial Pressing Machine with 50 kN. The dies set of steel has 1.5 cm diameter and 1.7 cm height. After that, drying was conducted using oven in temperature 200°C for 24 hours. Sintering was conducted right after that with different temperature of 1000, 1200, 1300 and 1400°C for 6 hours.

Porosity is a comparison between the open porous weight and total weight of the sample. Apparent porosity test refers to ASTM C-20 [8]. The value of porosity was calculated with:

\[
\text{Apparent Porosity} = \frac{V_0}{V} \times 100\% = \frac{W - D}{W - S} \times 100\% = \frac{W - D}{V} \times 100\% \quad (1)
\]

Cold crushing strength (CCS) test was conducted by giving one direction force to sample until crushed, using Uniaxial Pressure Machine. The value of CCS shows the ability of material to withstand on pressure in room temperature which refers to ASTM C133 [8]. The value of CCS was calculated with:

\[
\text{CCS} = \frac{F}{A} \quad (2)
\]

Wear resistance was conducted in abrading wheel with velocity of 90 rpm for 5 minutes. The value of wear resistance was the weight loss of each sample. Hydration resistance test was conducted for samples in sintering temperature of 1000°C. Samples were located in room with temperature of 25–30°C and relative humidity 68–82% [9]. The weight gain was calculated for 23 days.

Thermogravimetry Analysis/Differential Thermal Analysis (TGA/DTA) test was conducted for samples containing 2 wt.% Al + 3 wt.% Si and 5 wt.% Si antioxidants. The test was performed on the Setaram Setsys 1750 machine which operated up to 1300°C with a temperature rate of 10°C/min. X-Ray Diffraction (XRD) patterns were recorded using XRD Rigaku SmartLab machine with Cu Kα radiation. The samples tested were samples with the addition of 5 wt.% Al and 5 wt.% Si antioxidants at a sintering temperature of 1400°C. This test was performed to see the compounds that were formed. The microstructural evaluation of the sintered sample was performed by scanning electron microscopy (SEM) JEOL 6510. Samples containing 5 wt.% Al, 2 wt.% Al + 3 wt.% Si and 5 wt.% Si antioxidants were used for both tests in sintering temperature of 1400°C.
3. Results and Discussion

3.1. Thermal Characterization

In order to observe and identify the existence of organic phase, graphite and antioxidants containing in alumina spinel, thermal characterization was studied using TGA and DTA curves. It was predicted what process occurred during heating and identified the critical temperature of new phase formation. Fig. 1 shows TGA-DTA curves for samples containing 2 wt.% Al + 3 wt.% Si antioxidants. In temperature 100–400°C, water vaporization, phenolic resin decomposition, hydroxide and small compounds (e.g. CO, CO₂, CH₄) decomposition occurred [10-12], as weight loss shown in TGA curve. Fig. 2 for sample containing 5 wt.% Si shows the similar results as Fig. 1.

![Fig. 1. TGA-DTA curve for the refractory with 2 wt. % Al + 3 wt. % Si](image1)

![Fig. 2. TGA-DTA curve for the refractory with 5 wt. % Si](image2)
Fig. 1 shows graphite oxidation and Al oxidation into $\text{Al}_2\text{O}_3$ in temperature 500–800°C. In temperature 500–850°C, Al was melted and formed Al$_4$C$_3$ with graphite [11-13]. In temperature 1000°C, Si was oxidized into SiO$_2$, and graphite was still oxidizing to form more stable compound of CO. Carbide and oxide compounds were formed in temperature above 1000°C [10-17]. Fig. 2 shows the similar same results as Fig. 1. However, carbide and oxide compounds formation just occurred for Si elements. In temperature of 950°C, mullite was formed, as shown in XRD test as well.

3.2. Porosity, Mechanical and Hydration Properties

Antioxidants addition decreases the porosity in temperature more than 750°C [10]. Fig. 3 shows apparent porosity decreased along with sintering temperature increase as neck formation between solid particles occurred better. The event was supported by TGA-DTA curves showing weight gain occurred in temperature more than 750°C. According to TGA-DTA curves, weight loss in temperature of 200–850°C occurred because of binder decomposition and aluminum melting, and caused porosity formation in refractory. In temperature above 950°C, weight gain occurred because of oxide formation filling the porosity [9]. Sample containing 5 wt.% Al in 1400°C has the smallest value of porosity, 18.72%, caused by aluminum affinity to react with oxygen and graphite is higher than silicon. Therefore, oxide and carbide were formed better in samples containing higher aluminum addition.

Oxide and carbide compounds formation increased the cold crushing strength. Fig. 4 shows CCS increased along with sintering temperature increase as mass transfer in each particles that formed ceramics bonding occurred. Besides, neck formation between particles created bigger diameter [10]. Sample containing 5 wt.% Al in 1400°C has higher CCS than others, 39.33 MPa, caused by aluminum has lower melting point and ease to form Al$_4$C$_3$. The carbide will react with CO to form Al$_2$O$_3$ improving refractory strength [13]. The mechanism occurred as well in samples containing Si, yet required higher temperature.

![Apparent porosity vs. sintering temperature for the alumina spinel refractories with aluminum and silicon antioxidants addition](image-url)
Fig. 4. Variation in cold crushed strength with sintering temperature for the alumina spinel refractories with aluminum and silicon antioxidants addition

Wear resistance shows formed ceramics bonding strength to withstand on high speed of wear. Fig. 5 shows wear resistance, shown in weight loss, increased along with sintering temperature increase as sintering process occurred better in high temperature. In temperature of 1100°C, weight loss declined steeply because ceramics bonding formed stronger. Sample containing 5 wt.% Al in 1400°C shows the best result with weight loss of 0.0028 gr. The density plays an important role to increase the wear resistance. Therefore, aluminum addition increased wear resistance, better than silicon.

Fig. 5. Variation in wear resistance with sintering temperature for the alumina spinel refractories with aluminum and silicon antioxidants addition
Fig. 6 shows all samples adsorbed vapor as shown in weight gain every day. Sample containing 5 wt.% Al has the lowest resistance to hydration with %-weight gain 0.168%, while sample containing 5 wt.% Si has the best resistance with %-weight gain 0.071%. Al$_4$C$_3$ and Al$_2$O$_3$ in sample containing 5 wt.% Al reacted with vapor to form Al(OH)$_3$. The hydrate expanded and caused refractories disintegration [9]. On the other hand, silicon formed passive layer of gel M-S-H on refractory surface and prevented from vapor adsorption [18]. In the first three day, sample containing 5 wt.% Si had higher %-weight gain as the formation of passive layer occurred. After that, the weight gain did not occur significantly.

![Weight Gain](image)

Fig. 6. Weight gain as a function of adsorption days the alumina spinel refractories with aluminum and silicon antioxidants addition

### 3.3. Phase Composition and Microstructure

XRD test was conducted for samples containing 5 wt.% Al and 5 wt.% Si in sintering temperature of 1400°C. Fig. 7 shows the spinel and alumina dominated the compounds formed. Alumina was a result of oxidation process during sintering, indicating aluminum powder succeeded as the antioxidant. Fig. 8 shows some compounds beside alumina and spinel were formed, such as silica, mullite and silicon. The presence of Si element shows that silicon did not work well as antioxidant.

![Phase Composition](image)

SEM/EDS test was conducted for samples containing 5 wt.% Al, 5 wt.% Si and 2 wt.% Al + 3 wt.% Si. Fig. 9 shows the morphologies are granules in some area and flakes in another area. However, in Fig. 10, the morphologies are granules in most of the area and melted shape in different area. Fig. 9 shows EDS result for sample containing 5 wt.% Al where alumina dominated the compounds formed. The presence of graphite and magnesium were very low for both results. Fig. 11 shows several compounds were formed. The existence of alumina explains that aluminum powder worked well as antioxidant. Mullite compound was formed as well. However, silicon oxidation was not complete shown with Si existence.
Fig. 7. XRD pattern for alumina spinel refractory with addition of 5 wt.% Al

Fig. 8. XRD pattern for alumina spinel refractory with addition of 5 wt.% Si

Fig. 9. EDS analysis of sintered aluminum spinel refractory with addition of 5 wt.% Al
Fig. 10. EDS analysis of sintered aluminum spinel refractory with addition of 5 wt.% Si

Fig. 11. EDS analysis of sintered and polished aluminum spinel refractory with addition of 2 wt.% Al + 3 wt.% Si. The marked area indicates the dominant area of each of the compounds or elements that make up the refractory

The elemental mapping characterization shown in Fig. 12 and 13 for samples with the addition of 5 wt.% Al and 5 wt.% Si antioxidants, respectively. The most dominant observed element is aluminum. This is because the refractory raw materials used were commercial AR 90 with alumina composition of more than 87%. In Fig. 12, it shows that many oxide compounds were formed in the sample. Most regions are an association of elements of Al, Mg and O showing the spinel phase. In Fig. 13 there is an area which is an association of Si and O elements showing the silica phase. There is also an area which is an association of all elements indicating the presence of oxide and carbide phases. Areas that are only associated with C without additional elements indicate the presence of non-oxidized graphite.
4. Conclusions

The influence of Al and Si antioxidants on the mechanical properties, phase composition and microstructure was studied in this research. The main conclusions are as follows:

a. Alumina and spinel are the major compounds for sample containing Al while silica and mullite are the major compounds for sample containing Si.

b. Porosity decreased along with sintering temperature increase. Wear resistance and CCS increased along with sintering temperature increase. Sample containing 5 wt.% Al shows the best result for the tests.

c. Sample containing 5 wt.% Si shows the best result for hydration resistance test.
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6. References

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