Study on Hydration Resistance of MgAlON Composites

Yanqin Guo and Zhe Ji

Huanghe Science and Technology College, Zhengzhou 450063, China
Email: 27669932@qq.com

Abstract. Selected Aggregate, matrix and a small amount of sintering aids as raw materials. Mixed raw materials evenly, Sintered in high temperature nitriding furnace. Two test samples series of hydration resistance were made. Measured the pH value of the hydration samples, the content of nitrogen before and after hydration; drawn the change curve of pH value; calculated the weight change rate of samples before and after hydration; detected the phase composition of block sample before and after hydration. The results show that: under the same process conditions, the hydration resistance of MgAlON composite with spinel as aggregate is better than that of MgAlON composite with magnesia as aggregate. Compared with the sample of the same aggregate, the hydration resistance of the alumina based sample is better than that of the bauxite based sample. The phase composition of samples is almost unchanged before and after hydration, The reason for hydration is mainly due to the hydration of a small amount of AlN in the sample. The hydration resistance of MgAlON composites is much better than that of AlN composite.

1. Introduction
The materials are easy to be hydrated will undergo hydrolysis reaction, which is unfavorable to the storage and transportation of materials. The hydration reaction of the materials at high temperature may also lead to the limitation of their application scope, and even bring adverse consequences to the application of materials. Previous research found that MgAlON materials have excellent and benign properties such as high temperature resistance, high strength and corrosion resistance[1-4]. At present, there are many reports about the hydration resistance of AlN in the literature, and few reports on the hydration resistance of MgAlON (or AlON) and its composites prepared by aluminothermic nitriding. Therefore, it is of great practical significance to study the hydration resistance of MgAlON and its composites for the development and expansion of the application range of MgAlON and its composites. Therefore, this paper mainly studies the hydration resistance of MgAlON composite with magnesia as aggregate and MgAlON composite with spinel as aggregate, and compares the hydration resistance of bauxite based and alumina based MgAlON samples.

2. Experimental
The experimental materials selected are: (1) aggregate: fused magnesia alumina spine, high-purity fused magnesia; (2) matrix;(3) dextrin: binder. Table 1 is the composition of the sample.
Table 1. Formulations of the specimens

| Sample number | Aggregate | bulk material |
|---------------|-----------|---------------|
|               | MgO       | Al(<0.074 mm)- |
|               |           | bauxite (<0.088 |
|               |           | Al(<0.074 mm)- |
|               |           | Al₂O₃ (≤5μm) |
|               |           | MgO (≤0.04μm) |
| grain size    | 3-1mm     | 1-0 mm        |
|               | 3-1mm     | 1-0 mm        |
| YMM           | 45        | 15             | 40             |
| YJM           | 45        | 15             | 40             |
| FMM           | 45        | 15             | 40             |
| FJM           | 45        | 15             | 40             |

After mixing and testing the raw materials evenly, the samples will be pressed into strips (25 mm × 25 mm × 125 mm); the samples will be kept for 24 hours, and then nitrified and fired. After the samples are cooled, the samples will be divided into strips and the powder will be tested for water resistance. Select the powder and strip sample of particles and put them into the oven at 110°C. Dry the strip and powder samples, after natural cooling, weigh 5.00g of powder into the beaker, add 50ml of distilled water; weigh the weight of the strip sample, put it into the beaker, inject 10 times of distilled water into the beaker, stir the glass rod evenly, seal the cup mouth with plastic film, and then measure the pH value of the suspension every half an hour with pH meter. When the measured pH value of the strip sample fluctuates slightly (basically remains constant), take out the sample and put it into an oven at 110°C for drying. Analyze the change of phase composition before and after hydration with X-ray diffractometer, and determine the nitrogen content of the sample before and after hydration with chemical method.

3. Results and Discussion

3.1. Analysis of pH Value Change of Different Aggregate Samples

It can be seen from Figure 1 that the pH value of FMM suspension of powder sample rises from 7.45 to 8.23 in the first half hour, and reaches 10.02 in 12 hours. With the extension of time, the pH value is basically stable, and after 24 hours, the pH value is basically stable at about 10.12. The change rule of the pH value of bulk suspension with time is roughly the same as that of powder, but the difference is that the pH value does not change significantly in the first half hour. The pH value measured in this process is lower than that of powder.

![Figure 1. FMM pH curve changed with time](image1)

![Figure 2. FJM pH curve changed with time](image2)

It can be seen from Figure 2 that for sample FJM, the pH values of powder and bulk suspension increased from 7.45 to 8.53 and 7.83 respectively in two hours, and the pH values of the two suspension tended to be stable with the increase of time. During the whole measurement process, the
pH values of bulk samples were about 0.6 lower than that of powder samples, and tended to be stable 24 hours later.

Comparing the pH value of powder sample and block sample, it can be seen that the pH value of suspension of powder sample is significantly higher than that of block sample. Obviously, the hydration resistance of block sample is better than that of powder sample, which is mainly due to the large specific surface area of powder sample.

It can be seen from Fig. 3 and Fig. 4 that the overall trend of hydration of the four groups of samples is basically the same: the pH value increases gradually with the increase of time, changes slowly after 12 hours, and the pH value is basically stable after 24 hours. It can be seen from the hydration trend of the first two hours that the pH value changes obviously in the first 0.5 hours, and the rising trend of pH value with time does not change obviously after that, so it can be seen that the material has good hydration resistance. It can be seen from the analysis of figures 3 and 4 that the pH change curve of magnesia aggregate sample is slightly higher than that of spinel aggregate sample, mainly because the magnesia material itself is not as dense as spinel material; compared with the samples of the same aggregate, the pH value of oxide based sample is slightly higher than that of bauxite based sample, and the presence of impurities in bauxite will affect the hydration resistance of the sample.

The hydration mechanism of the composite was analyzed. The pH value of the solution increased rapidly from 5.5 to about 7.5 in the first 10 minutes of the powder. The reason for the rapid rise of pH value was that the ammonia produced by AlN hydrolysis was dissolved in the water. After that, with the extension of time, the pH value did not change much, which was due to the hydrolysis speed of AlN slow down. The chemical reaction formula of AlN powder with water is as follows (1-3). A layer of amorphous AlOOH or crystalline Al(OH)₃ is formed on the surface. The AlO0.5N0.6 compound produced is a component of the sub surface, and the AlN core is in its center.

\[
\begin{align*}
\text{AlN} + 2\text{H}_2\text{O} &\rightarrow \text{AlOOH}_{\text{amorph}} + \text{NH}_3^+ \quad (1) \\
\text{NH}_3 + \text{H}_2\text{O} &\leftrightarrow \text{NH}_4^+ + \text{OH}^- \quad (2) \\
\text{AlOOH}_{\text{amorph}} + \text{H}_2\text{O} &\rightarrow \text{Al(OH)}_3 \quad (3)
\end{align*}
\]

In addition, for magnesia refractories, it is also necessary to take into account the formation of hydroxides after the moisture absorption of MgO in the atmosphere, so as to make the products loose and damaged. The chemical reaction formula is as follows:

\[
\text{MgO} + \text{H}_2\text{O} \rightarrow \text{MgO(OH)}_2 \quad (4)
\]

In order to improve the hydration resistance of the material, the first step is to promote sintering, reduce porosity and increase density. At the same time, a protective layer should be added to reduce
the contact with the atmosphere. Its purpose is to extend the storage time of products and improve the service life of materials. In addition, for MgAlON composite, it is necessary to reduce the AlN content in the product as much as possible to improve the hydration resistance of the material.

3.2. Comparative Analysis of Weight Change Rate and Nitrogen Content of Sample after Hydration

In order to better inspect the hydration resistance of the sample, the weight change and nitrogen content of the sample before and after oxidation are measured by weight method and chemical analysis method respectively, and the weight change rate and nitrogen content of the sample before and after hydration are calculated. The results are shown in Table 2. Through comparative analysis of weight and N content changes of samples before and after hydration, it can be seen from Table 2 that: after hydration, the hydration weight gain rate and nitrogen content loss rate of magnesia aggregate samples are greater than those of spinel aggregate samples; compared with the same aggregate samples, the nitrogen content loss rate of bauxite based samples is greater than that of alumina based samples. On the one hand, the structure of magnesia aggregate sample and bauxite based sample is relatively loose, the sintering performance is relatively poor, on the other hand, magnesia itself has a certain degree of hydration.

### Table 2. Weight changing rate and the N content of the hydrated and unhydrated block specimens

| Sample number | Unhydrated weight (g) | Nitrogen content (%) | Hydrated weight (g) | Nitrogen content (%) | Weight gain rate (%) | Nitrogen content loss rate (%) |
|---------------|-----------------------|----------------------|---------------------|----------------------|----------------------|-----------------------------|
| YMM           | 10.96                 | 2.9                  | 11.01               | 2.51                 | 0.45                 | 13.45                       |
| FMM           | 11.2                  | 3.57                 | 11.24               | 2.77                 | 0.34                 | 22.41                       |
| YJM           | 11.26                 | 5.21                 | 11.32               | 5.02                 | 0.53                 | 3.74                        |
| FJM           | 12.06                 | 6.03                 | 12.10               | 5.37                 | 0.32                 | 10.95                       |

In conclusion, the hydration resistance of spinel based sample is better than that of magnesia based sample, and that of bauxite based sample is worse than that of alumina based sample.

3.3. Comparative Analysis of Phase Composition of Samples Before and after Hydration

X-ray diffractometer is used to analyze the phase composition of massive samples before and after hydration, as shown in Figure 5.

![Figure 5. XRD patterns of the hydrated and unhydrated specimens](image-url)
According to the XRD pattern in Fig. 5, it can be seen that the phase composition of the sample before and after hydration has little change. Except for the main crystal phase (mm series is periclase phase, JM series is magnesia alumina spinel phase), there are still MgAlON phase and a small amount of Al8O3N6 phase. Therefore, the hydrolysis mechanism of MgAlON composite is different from that of AlN, which is related to the hydrolysis mechanism of AlN polymorph.

4. Conclusion
Under the same process conditions, compared with the hydration resistance of different aggregate samples, the MgAlON composite with spinel as the aggregate is better than the MgAlON composite with magnesia as the aggregate;The hydration resistance of alumina based samples is better than that of bauxite based samples;The main reason of hydration is due to the hydration of a small amount of AlN polymorphs in the sample.

5. References
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