

Effect of spinel content on the properties of phosphoric acid bonded high alumina castables

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Abstract: In order to study the effect of fused spinel on the properties of phosphoric acid bonded high alumina castables, samples with different contents of fused spinel were prepared. The results show that when the contents of the fused spinel are between 8% and 16% (mass fraction), the castables have good properties. The castables overcome the shortages of the phosphoric acid bonded high alumina castables with bauxite cement as a hardening promoter. The experiments demonstrate that most of the service properties of the castables with fused spinel are better than those of the normal phosphoric acid bonded castables which use bauxite cement as a hardening promoter. The examination of the materials indicates that free MgO inclusions in the spinel powder can promote the hardening of the castables.

Key words: fused spinel; high alumina castables; phosphoric acid

1 Introduction

Castables have been progressively gaining market share in all areas of refractory application by replacing conventional firebricks and ramming mixes [1-4]. The phosphoric acid bonded high alumina castables possess high strength at medium temperature, excellent thermal shock resistance and abrasive resistance. Bauxite cement is generally used as a hardening promoter in the traditional phosphoric acid bonded high alumina castables. However, the amount of bauxite cements is difficult to control. The larger amount of bauxite cement will make casting difficult due to the quick coagulation. In reverse, the less amount of bauxite cement will make the castables coagulation too slow to get any significant strength. The castables could not obtain strength until they are heated up to 300°C. Therefore, the application of the castables has been limited despite they possess some excellent properties.

In this investigation, an attempt was made to use fused spinel instead of high alumina cement as a

hardening promoter and an additive in phosphoric acid bonded bauxite castables. The relationship between properties of high alumina castables and spinel content was systematically studied. A comparative research was done between the traditional phosphoric acid bonded high alumina castables and the castables with spinel as a hardening promoter and additive with respect to bulk density, Al₂O₃ content, refractory quality, compressive strength, flexural strength, thermal shock resistance and water resistance.

2 Materials and experimental procedure

2.1 Raw materials

The materials used in this work are phosphoric acid as a binder, sintered super-grade bauxite (Yangquan, Shanxi Province) as refractory aggregates and fine bauxite as refractory powder. In addition, fine fused spinel (Meihekou, Jilin Province) or bauxite cement are used as hardening promoters or additives. The chemical composition of raw materials is listed in **table 1**.

Table 1 The chemical composition of bauxite and fused spinel (mass fraction)

Additives	Al ₂ O ₃	SiO ₂	CaO	MgO	Fe ₂ O ₃	Na ₂ O	K ₂ O	TiO ₂	%
Bauxite	88.90	5.90	0.09	0.12	0.95	0.01	0.03	3.52	
Fused spinel	56.73	0.84	0.51	41.63	0.17	0.12	0.05	0.04	

2.2 Optimum grain grading

One of the important methods to improve the den-

sity, strength and abrasive resistance of the castables is to optimize the size distribution of the aggregate

and powder. Due to the difference in processing, the raw materials in different grade regions have different size distributions. In this work, four different kinds of particles of sintered super-grade bauxite were chosen, *i.e.* coarse particles (3-5mm), medium sized particles (1-3 mm), fine particles (0-1 mm) and fine powder (<0.04 mm). Fine spinel powder was used (<0.04 mm). The total contents of coarse and medium particles

were kept at 55% (mass fraction) and the ratio of the coarse particles to the medium particles was 1:1. The grading optimization was lied on the proportion of the fine particles and fine powders, so when the amount of the fused spinel powder was fixed at 10% (mass fraction), the optimization was done by changing the proportion between high alumina fine powder and fine particles.

Table 2 Size distribution of bauxite and spinel

Items	Size distribution (mass fraction) / %					Bulk density / g·cm ⁻³
	3-5 mm coarse particles*	1-3 mm medium particles*	0-1 mm fine particles*	<0.04 mm fine powder*	<0.04 mm spinel /%	
A	27.50	27.50	21.00	14.00	10.00	2.85
B	27.50	27.50	23.00	12.00	10.00	2.88
C	27.50	27.50	25.00	10.00	10.00	2.92
D	27.50	27.50	27.00	8.00	10.00	2.94
E	27.50	27.50	29.00	6.00	10.00	2.93
F	27.50	27.50	31.00	4.00	10.00	2.89
G	27.50	27.50	33.00	2.00	10.00	2.84

Note: * high alumina raw materials.

Table 2 shows the relationship between density and grain grading. It could be seen that the samples have the highest density when 0-1 mm fine particles content is 27% and the total content of the bauxite fine powder and the spinel powder is 18%.

2.3 Procedure

Castables were cast with the aid of vibrating table. In order to avoid the reaction between phosphoric acid and the ferrous phases in the bauxite to produce gas which may cause the density decrease of the samples, NH-66 was used as acid inhibitor [5]. Castables were cured in air at ambient temperature for 3 days and then dried at 110°C for 24 h. The samples were heated at a rate of 5°C·min⁻¹ from ambient temperature to 1300°C or 1500°C and kept at such temperatures for 10 h, respectively. The phosphoric acid bonded alumina castables with bauxite cement as a hardening promoter were fabricated in the same way and under the same condition.

The flexural strength, the compressive strength and linear change of green body and fired samples were measured. All data were obtained by taking the average value of three samples. The crushed samples were examined by XRD (X-ray Diffraction) to determine the phases. Thermal shock resistance of the prepared castables was measured according to Chinese standard YB2206-77 and refractory quality was determined according to Chinese standard YB/T5199.

3 Results and discussion

3.1 Physical properties

Based on D in table 2, eight group samples were

prepared (**table 3**) in order to study the effect of the fused spinel as a hardening promoter and an additive on the properties of high alumina castables. The fused spinel contents were changed from 4% to 18% and the high alumina fine powders varied correspondingly.

The samples were cured in air for 3 days, dried at 110°C×24 h, fired at 1300°C×10 h and 1500°C×10 h, respectively. Then the flexural strength, the compressive strength and linear change of the samples were tested. The results are shown in **figure 1**. Figure 1(a) shows that the flexural strengths of the castables after cured in air for 3 days increase non-linearly with the increase of the spinel content. This change can be explained by the reaction that takes place between phosphoric acid and spinel. When the amount of spinel is less than 6%, which is too less to react with the phosphoric acid completely, a significant polymerization of phosphates can not happen, the strength of the samples is very small. When the amount of spinel is higher than 8%, the strength enhances very rapidly but when the amount of the spinel is higher than 16%, the increase of strength becomes slow. When the amount of the spinel is too large, the castables harden too quickly and degrade its flow property correspondingly. These result in defects in the castables and make the strength increase slowly. The linear changes of all the samples are positive values. This behavior not only contributes to the improvement of the strength but also compensate the shrinkage to generate when the castables are dried and fired. The flexural strength and the compressive strengths of all the samples dried at 110°C are higher than those of the samples cured for 3 days. Compared with the samples cured in air for 3

days, all of the samples dried at $110^{\circ}\text{C}\times 24\text{ h}$ have higher strength. Even though the strength of these samples increases generally along with the increase of the spinel content in the samples, the increasing rate is not evenly distributed. As shown in figure 1(b), the strength stop increasing when the spinel content is more than 15%, and even slightly decreases when the spinel content is more than 16%. All the samples dried at $110^{\circ}\text{C}\times 24\text{ h}$ have a small negative value of linear change. As shown in figure 1(c), all the samples fired at $1300^{\circ}\text{C}\times 24\text{ h}$ have much higher strength than the samples dried at $110^{\circ}\text{C}\times 24\text{ h}$. Similar to the samples dried at $110^{\circ}\text{C}\times 24\text{ h}$, both compressive strength and

flexural strength increase with the increase of spinel in the samples, but the increasing rate is small. The maximum strength can be obtained when the samples contain 16% spinels. Taking the length of the samples dried at $110^{\circ}\text{C}\times 24\text{ h}$ as initial length, all the samples fired at $1300^{\circ}\text{C}\times 10\text{ h}$ have a linear change of small positive values. Figure 1(d) is the relationship of strength and the spinel content of samples fired at $1500^{\circ}\text{C}\times 10\text{ h}$. It is clear that the compressive strengths are much higher for these samples. But the flexural strengths do not increase much comparing with the samples fired at $1300^{\circ}\text{C}\times 10\text{ h}$. The linear changes are mostly small negative values.

Table 3 Size distribution of bauxite and different amount of spinel

Sample group	Size distribution of bauxite (mass fraction) / %					
	3-5 mm coarse particles*	1-3 mm medium particles*	0-1 mm fine particles*	<0.04 mm fine powder*	<0.04 mm spinel / %	40% phosphoric acid (extra) / %
1	27.5	27.5	27.0	14.0	4.0	14.0
2	27.5	27.5	27.0	12.0	6.0	14.0
3	27.5	27.5	27.0	10.0	8.0	14.0
4	27.5	27.5	27.0	8.0	10.0	14.0
5	27.5	27.5	27.0	6.0	12.0	14.0
6	27.5	27.5	27.0	4.0	14.0	14.0
7	27.5	27.5	27.0	2.0	16.0	14.0
8	27.5	27.5	27.0	0.0	18.0	14.0

Note: * high alumina raw materials.

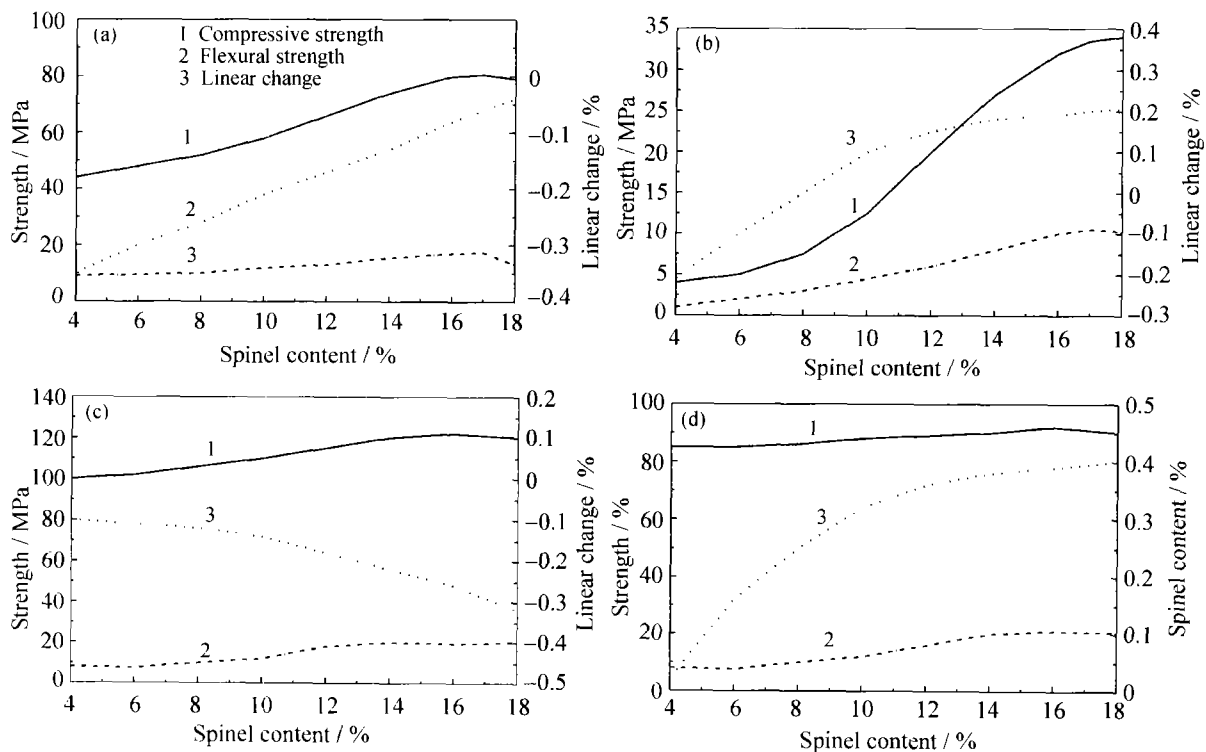


Figure 1 The effect of fused spinel content on the properties of samples, (a) cured in air for 3 days; (b) dried at $110^{\circ}\text{C}\times 24\text{ h}$; (c) fired at $1300^{\circ}\text{C}\times 10\text{ h}$; (d) fired at $1500^{\circ}\text{C}\times 10\text{ h}$.

Figure 2 shows the thermal shock resistance and refractoriness of the investigated samples. The thermal shock resistance of the samples improves very quickly

when the amount of spinel increases. Refractoriness of the samples decreases a little with the increase of the amount of spinel. This is probably because that there

is a little SiO_2 in the super-grade bauxite and it is easy to react with MgO , CaO and Al_2O_3 to produce the phases with low melting point.

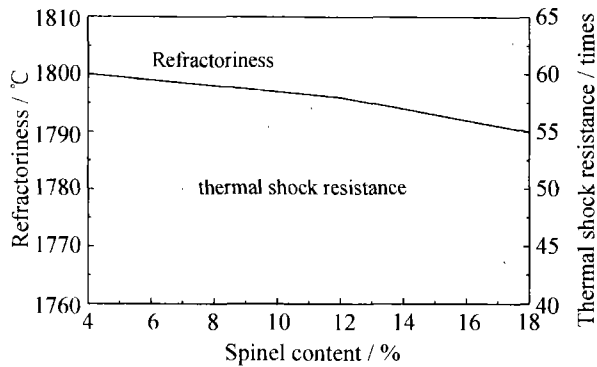


Figure 2 The thermal shock resistance and refractoriness of the investigated samples.

Table 4 shows the properties of the phosphoric acid bonded high alumina castables with different hardening promoters: (a) fused spinel, (b) bauxite cement.

Table 4 The properties of phosphoric acid bonded high alumina castables

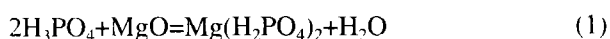
Hardener	Density / ($\text{g}\cdot\text{cm}^{-3}$)	Al_2O_3 content / %	Refractoriness/ °C	High temperature resistance* /°C	Water resistance (cured for 3 d)	Water resistance (cured for 3 d)
(a)	2.91	77.2	1790	1650	62	Good
(b)	2.78	77.5	1790	1450	30	Bad

Hardener	Strength after cured for 3 d in air /MPa		Strength after dried at 110°C×24 h /MPa		Strength after fired at 1300°C×10 h /MPa		Strength after fired at 1500°C×10 h /MPa	
	Flexural strength	compressive strength	Flexural strength	compressive strength	Flexural strength	compressive strength	Flexural strength	compressive strength
(a)	7.8	32.5	10.8	45.7	20.2	84.6	20.2	120.8
(b)	0.5	3.5	6.7	22.4	10.8	40.3	13.2	60.8

Note: (a) spinel as a hardening promoter and an additive (11%); (b) bauxite as a hardening promoter (2.5%); * temperatures at which the samples were fired for 3 h and their linear changes are less than 1.0%.

3.2 The roles of the fused spinel and reaction mechanism

Spinel with an ideal composition of $\text{MgO}\cdot\text{Al}_2\text{O}_3$ is an inert mineral. It does not react with any acid or alkali at room temperature. So spinel mineral itself can not be used as the hardening promoter of the phosphoric acid bonded castables. XRD diffraction pattern of the fused spinel (figure 3) shows that there exists a small amount of periclase, so the periclase (free MgO) in fused spinel react with phosphoric acid and promote hardening of the castables.



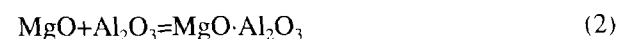
$\text{Mg}(\text{H}_2\text{PO}_4)_2$ is easy to form $n\text{Mg}\cdot 2n\text{PO}_3$ polymer and make the castables possess strength.

When the samples are dried at 110°C, the reaction is accelerated and lead to a rapid increase of the strength of the castables.

The results demonstrate that the hardening promoter has a significant and direct influence on the properties. Compared to the traditional phosphoric acid bonded high alumina castables, the castables with fused spinel as a hardening promoter and an additive possess higher strength and higher temperature resistant ability. Its maximum service temperature can be 200 °C higher than that of traditional castables. Meanwhile, the castables with fused spinel as a hardening promoter and an additive can develop high strength before drying and firing, the cured samples possess good ability of water resistance, but the traditional castables can not achieve. Such characters provide a great convenience for both on site casting and forming, and the transportation and storage of pre-formed refractory components. Its excellent thermal shock resistance can prolong its service lifetime effectively under a hard service condition where the temperature changes frequently and violently.

3.3 Phases of the phosphoric acid bonded high alumina castable with spinel as a hardening promoter and an additive

Figure 4 gives XRD diffraction patterns of the samples after fired at 1500°C. Corundum (Al_2O_3) and spinel (MgAl_2O_3) are the main phases in the sintered castables and no other mineral phases are detected. The small amount of SiO_2 and other impurities in raw high alumina bauxite have entered into glass phases while the periclase in the fused spinel reacted with alumina in the bauxite to form new spinel phase.



The reaction accompanies with volume expansion, which could compensate for some content due to the volume shrinkage during the firing process at elevated temperature.

Because the fused spinel is added as fine powder

and the reaction (1) and (2) consumes some bauxite powder, the matrix of the castables is mainly spinel phase after being fired. It is well known that self-forming spinel often have better resistance to slag penetration and corrosion, so this lead the castables to have superior slag resistant ability [6-10]. Moreover, when a small amount of melt is produced in the castables at high temperature, some MgO would dissolve into glass and the glass phase itself could have a composition similar to cordierite. So the cordierite mineral would crystallize from the glass phase during the process of temperature decrease or repeated heating and cooling. Cordierite has an extremely low thermal expansion rate. Spinel also has a very low thermal expansion rate comparing with corundum, so the ability of thermal shock resistance of the castables is improved greatly.

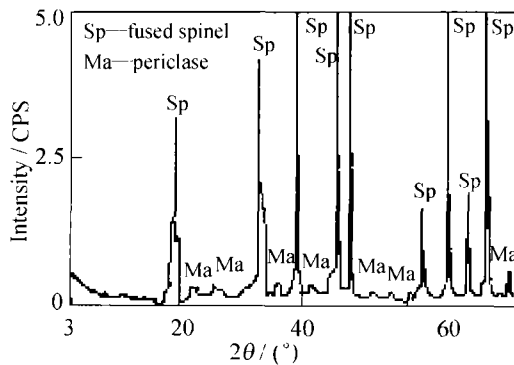


Figure 3 XRD diffraction pattern of fused spinel powder.

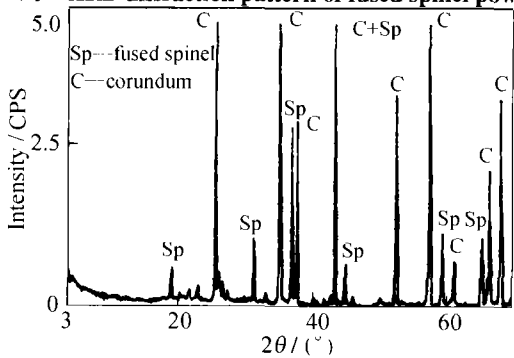


Figure 4 XRD diffraction pattern of samples after fired at 1500°C.

4 Conclusion

The phosphoric acid bonded high alumina castables with excellent properties can be made when super-grade bauxite is used as aggregates, phosphoric acid

as a binder, fused spinel powder as a hardening promoter and an additive. This castables is very strong after cured for 3 days in air, dried at 110°C and fired at elevated temperatures. Its maximum service temperature can be as high as 1650°C. The periclase inclusion exists in the fused spinel. It is the major contributor to the function of hardening promotion of the spinel powder. The controlled reaction enables the castables have longer period to harden which makes it easier to be cast and formed on site.

References

- [1] S. Banerjee, *A Comprehensive Handbook on Monolithic Refractories* [M], The American Ceramic Society, Westerville, 1998.
- [2] C.F. Chan and Y.C. Ko, Influence of coarse aggregate content on the thermal conductivity of alumina-spinel castables [J], *J. Am. Ceram. Soc.*, 79(1996), No.11, p.2916.
- [3] Emmanuel Nonnent, Nicolas Lequeux, and Philippe Boch, Elastic Properties of High Alumina Cement Castables from Room Temperature to 1600°C [J], *J. Eur. Ceram. Soc.*, 19(1999), p.1575.
- [4] S. Mukhopadhyay, S. Ghosh, and M.K. Mahapatra, Easy-to-use and spinel sols as bonding agents in a high-alumina based ultra low cement castable [J], *Ceram. Int.*, 28(2002), p.719.
- [5] Zhongcheng Wang and Xiankun Zhang, The application of NH-66 acid inhibitor on the phosphoric acid bonded high alumina castables [J], *Refractory*, 25(1991), p.121.
- [6] Y. Urita, M. Sugawara, M. Kataoka, and K. Yamaguchi, Development of self-forming spinel castable for steel ladle, [in] *39th Int. Coll. on Refr. in "Stahl & Eisen spezial"* [C], 10(1996), p.108.
- [7] M. Fuhrer, A. Hey, and W.E. Lee, Microstructural evolution in self-forming spinel/calcium aluminate-bonded castable refractories [J], *J. Eur. Ceram. Soc.*, 18, (1998), P.813.
- [8] P. Korgul, D.R. Wilson, and W.E. Lee, Microstructural analysis of corroded alumina-spinel castable refractories [J], *J. Eur. Ceram. Soc.*, 17(1997), p.77.
- [9] H. Sumimura, T. Yamamura, and Y. Kubota, *et al.*, Study on slag penetration of alumina-spinel castable, [in] *Proc. UniteCR 91* [M], 2(1991), p.138.
- [10] M.W. Vance, G.M. Kriechbaum, and R.A. Henrichsen, *et al.*, Influence of spinel additives on high alumina/spinel castables [J], *Bull. Am. Ceram. Soc.*, 73(1994), p.7.