EFFECT OF ADDING A KIND OF SURFACTANT ON PORE SIZE DISTRIBUTION AND PROPERTIES OF ALUMINA-SPINEL CASTABLE

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ABSTRACT

A kind of surfactant was introduced into alumina-spinel castable for making steel ladle integral purging plugs by pre-casting for the purpose of avoiding big pores and improving properties. The surfactant was absorbed by alumina based powders by pre-mixing them, so that it can be better dispersed in the castable by adding such powdery additive. The addition was set at 0, 1%, 2% and 3% respectively. Properties of the castables in terms of water demand, flow value, hot modulus of rupture and permanent linear change were investigated and microstructure of the samples after hot strength test were observed by SEM. The incorporation of such agent can influence the flow behavior, properties and microstructure of the castables, while little effect on the original shaping and drying process as well as volumetric stability at high temperature. The introduction of this additive is helpful to reducing bleeding phenomenon of the castable and avoiding segregation. Hot modulus of rupture at 1400℃ can also be enhanced from 14.3 MPa to 16.8 MPa at 1% addition of the additive, which can be attributed to a reduction of big vacancies and an increase in smaller size pores more uniformly distributed in the matrix. Field test of the improved alumina-spinel castable with addition of 1% of the additive was carried out as pre-cast integral purging plugs in a 90t stainless steel ladle in Taiyuan Iron & Steel (Group) Co., Ltd. and positive results were obtained, evidenced by reduced late stage cracking and prolonged durability.

KEY WORDS: Surfactant, pore, Alumina-spinel Castable, Strength, Microstructure

INTRODUCTION

As a part of structural composition, pores are closely associated with properties, quality consistency and service performance of refractories. For the alumina-spinel castable for making steel ladle integral purging plugs, pores are believed to be an important factor affecting hot strength and thermal shock resistance, as key properties to achieve good service performance. Pore-relating characteristics usually include porosity, pore shape, size and distribution. Pores in refractories are closely related to processing factors in addition to those introduced by raw materials. For refractory castable, a proper amount of liquid substance, water in most cases, is necessary to reach a requested flowability. However, it is worth our attention that flowability should not be treated as equal to whole flow behavior. An appropriate flow behavior also includes softness, degassing and segregation behaviors of the wet mixes during vibration casting process, besides requested flowability, which can be obtained by optimal particle size distribution and adopting suitable dispersing agent and surfactant.

In this work, a kind of surfactant was incorporated into alumina-spinel castable for the purpose of achieving more homogeneous structure and better properties by avoiding big pores without negatively affecting the liquidity and shaping process.

EXPERIMENTAL

The adopted raw materials in this work include tabular alumina aggregates (8~5mm, 5~3mm 3~1mm and 1~0mm), tabular alumina fines under 325 mesh, sintered spinel (1~0mm and -325 mesh), alumina ultra fines (1~2 μm), calcium aluminate cement and specific organic dispersants. The adopted surfactant, aiming to facilitate the formation of a better distributed and widespread microstructure and microporosity in refractories, has been pre-mixed with alumina powders in proportion of 1:9 and then introduced by adding such powdery additive, marked as SMB-2 in this work.

An alumina-spinel castable, coded as AS, for making steel ladle integral purging plugs was selected as a reference. The addition of the powdery additive SMB-2 was set at 0, 1%, 2% and 3% respectively as shown in Tab. 1.

Tab. 1: Recipes of alumina-spinel castables with different surfactant additions (wt%)

Raw material	AS0	AS1	AS2	AS3
Tabular alumina	60	60	60	60
Tabular alumina fines	14	13	12	11
Sintered spinel	15	15	15	15
Alumina ultra fines	6	6	6	6
CA Cement	5	5	5	5
SMB-2	0	1	2	3

Specimens of 40mm × 40mm × 160mm were prepared through a general vibration casting process, at a water addition of 4 wt%. After demolding and naturally curing for 1d, the specimens were dried at 110℃ for 24h and then heated at 1400℃ and 1600℃ respectively for 3h in a muffle furnace.

Hot modulus of rupture (HMOR) at 1400℃ for 1h was tested on the specimens after dried. Bulk density, cold crushing strength (CCS), cold modulus of fracture (CMOR) and permanent linear change (PLC) were also tested. The uniformity of the structure and pore size and distribution in the matrix of samples after HMOR test were observed by SEM.

RESULTS AND DISCUSSION

The flowability characterized by vibration flow value of the castables with different surfactant addition varies from 198mm to 168mm with the increase of SMB-2 addition, as shown in Fig.1.

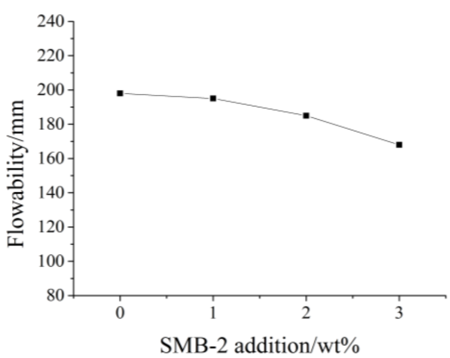


Fig. 1: Vibration flowability of the castables vs. SMB-2 addition

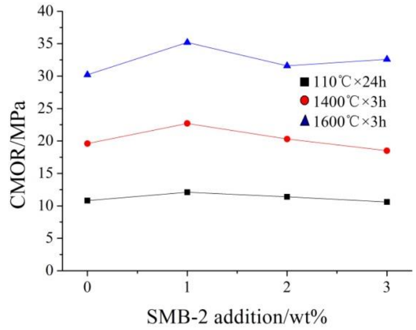
As seen, the flowability remains acceptable when the powdery additive addition is under 2%. However, significant difference in flow behavior can be found between the wet mixes with more than 2% of SMB-2 addition and that, i.e. AS0, without the additive.

Fig. 2: Surface outlook of the mixes with different surfactant addition after vibration casting

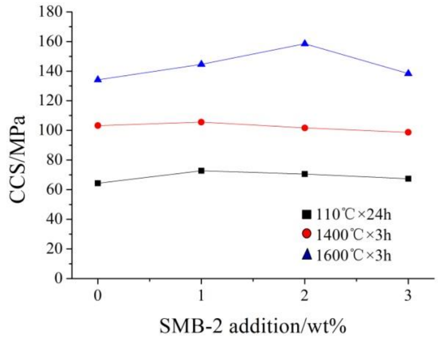
Fig. 2 shows surface outlook of the different mixes after vibration casting and standing for about 20min. AS0 mix exhibits a serious bleeding phenomenon with clear water precipitation on the surface after shaping. With quite an equivalent flowability, less bleeding phenomenon is seen for AS1 mix with 1% of SMB-2 addition, implying less segregation and more homogeneous internal structure.

As well known, strength is a certain function of structure in which pore size and distribution are involved. The introduction of surfactant is expected to optimize flow behavior of the wet mixes and pore structure in their green body.

Fig. 3 illustrates the cold strengths of the castable specimens after dried at 110℃ and heated at 1400℃ and 1600℃ respectively. There is an interesting discovery here. The incorporation of SMB-2 exhibits little influence on the cold strengths after drying, but more evident after being heated at high temperature, in particular at 1600℃, like in the cases of AS1 and AS2, with highest CMOR and CCS respectively.



(a) CMOR



(b) CCS

Fig. 3: Cold strengths of the castables vs. SMB-2 addition

Cold strengths such castables after drying depend greatly on the added water amount and hydraulic reaction of the CA cement. The fact that little change in this stage's strength with increasing surfactant addition means the added surfactant has little effect on the cement hydration, nevertheless it can obviously change the flow behavior. For specimens after heated at high temperature, reactions are finished in the matrix, and then the strengths depend mainly on the fatal structure defects like big pores. Accordingly the role of surfactant in big pore reduction and strength enhancement becomes apparent.

HMOR of the alumina-spinel castables at 1400℃ for 1h is shown in Fig. 4.

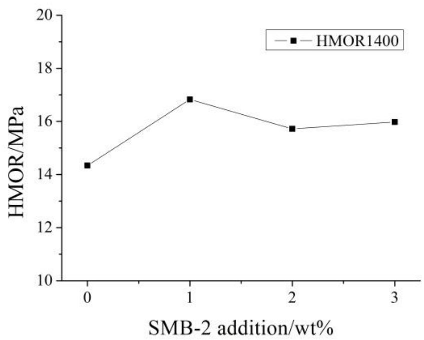


Fig. 4: HMOR at 1400℃ for 1h of the castables vs. SMB-2 addition

HMOR has been enhanced form 14.3MPa to 16.8MPa by incorporation of 1% of SMB-2 additive. Although some negative effect is seen on flowability when the additive addition above 2%, the hot strength of AS3 specimen is still higher than that of AS0's. This favorable effect can also be attributed to the improved microstructure with reduced big pores, thanks to the added surfactant.

As seen in Fig. 5, volumetric stability characterized by PLC of the castables after firing at high temperatures changes little as the surfactant addition increases.

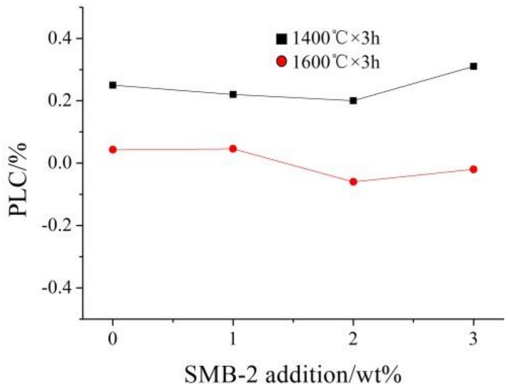


Fig. 5: Permanent linear change of the castables vs. SMB-2 addition

All the castables exhibits slight residual expansion, with PLC values ranging from 0 to 0.25% after heated at 1400℃ and 1600℃. It is believed that PLC is mainly affected by the matrix interaction related to chemical and mineralogical compositions. The incorporated surfactant does not change the total composition and shaping process, so little effect is found on PLC, being some influence on bulk density as shown in Tab. 2.

Tab. 2: Bulk density of the castables after drying vs. SMB-2 addition (g/cm^3)

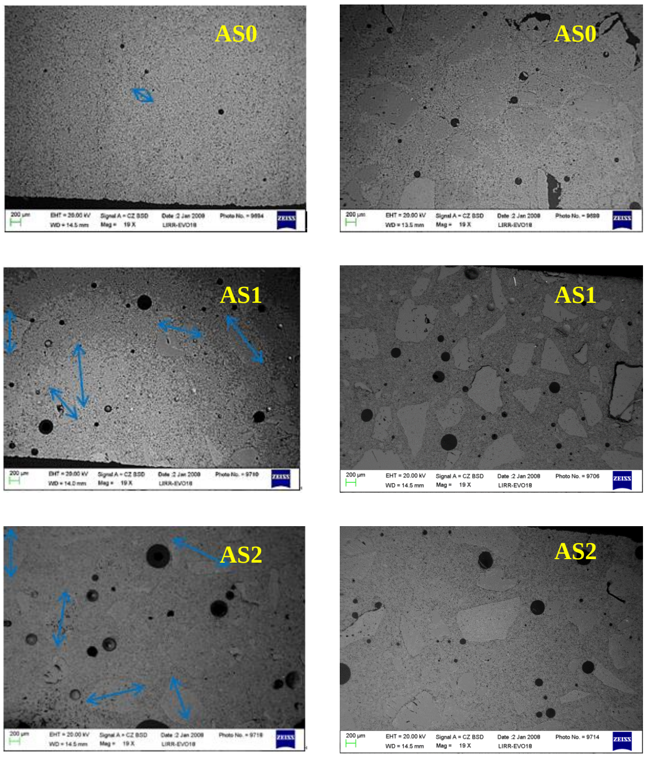
No.	AS0	AS1	AS2	AS3
Bulk density	3.10	3.10	3.11	3.12

Microstructure analysis was carried out by means of SEM on samples AS0, AS1 and AS2 after HMOR tests to investigate the effect of adding the surfactant on microstructure of the castables.

Fig. 6 shows structural difference between surface area and interior area with about 15mm depth form shaping surface. The difference can well reflect the segregation degree of the alumina-spinel castables.

For sample AS0 without the surfactant addition, there are few aggregates marked by blow double arrow in shaping surface area, exhibiting a clear difference with the structure in deeper zone, which derives from bleeding phenomenon and segregation in casting process. In great contrast to AS0, samples incorporated with the surfactant like AS1 and AS2 possess more homogeneous structure in the different zones. In addition, there are more small bubbles located in the castable originated from the water added. The presence of such bubbles is believed to be beneficial to thermal shock resistance and thermal insulation of the castables.

Surface features of raw materials and the wetting between the feedstock and water can be influenced by the added surfactant and so on pores characteristics in the matrix too. As evidenced by Fig. 7, the size and its distribution homogegeneity of pores in the matrix are quite different in these three samples.



(a) Shaping surface (b) Interior area

Fig. 6: Structure comparison between surface and interior area of samples AS0, AS1 and AS2

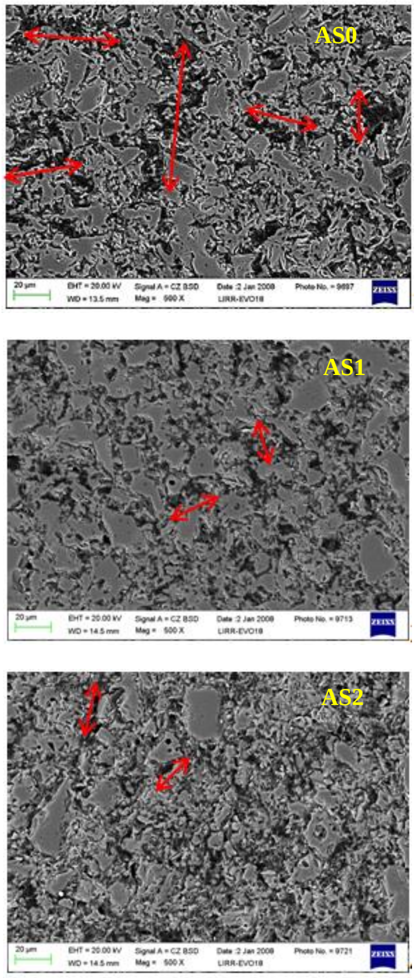


Fig. 7: Pores distribution in the matrix of samples AS0, AS1 and AS2

Pores, marked by red double arrow, in the matrix of sample AS0 are bigger and longer than those in samples AS1 and AS2. The longest pore defect dimension in AS0 is close to 100 microns while only about 30 microns in AS1 and AS2. Less big pores and better structural homogeneity imparted from the surfactant are certainly helpful to the improvement in strength properties of the castables.

Field test of 4 pieces of purging plugs pre-cast by using the improved alumina-spinel castable with addition of 1% of the surfactant additive was carried out in a 90t stainless steel ladle in Taiyuan Iron and Steel (Group) Co., Ltd. Positive results were obtained, evidenced by reduced late stage cracking and prolonged service life from averaged 72 to 80 heats.

CONCLUSIONS

Incorporation of suitable surfactant can influence flow behavior, microstructure and properties of the investigated alumina-spinel castable, while little effect on the original shaping and drying process as well as volumetric stability fired at high temperature.

Microstructure featured by reduced big vacancies and increased smaller size pores more uniformly distributed in the matrix can be obtained by adding the surfactant. The positive effect on microstructure is beneficial to enhancing cold and hot strengths. An addition of 1~2% such surfactant is suggested compromisingly.

Reduced cracking and prolonged working life by more than 10% of purging plug made by using the improved alumina-spinel castable with addition of 1% of the surfactant additive has been achieved in a 90t stainless steel ladle.