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High temperature mechanical properties of bauxite-based SiC-containing castables

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Abstract

High temperature strength and thermal shock resistance of ultra-low cement bauxite-based SiC-containing castables with two different ultra-fine alumina/microsilica ratios (Al_2O_3/SiO_2 = 25/75 and 75/25) have been studied. The results show that SiC addition in the range from 4 to 16% is beneficial to improvement of mechanical properties as well as thermal shock resistance, and its effect may be correlated with microstructural features of the castables.

Keywords: C. Mechanical properties; C. Thermal shock resistance; E. Refractories

1. Introduction

The attractiveness of low cement and ultra-low cement bauxite castables for refractory applications is due not only to their high strength, thermal shock resistance and corrosion resistance, but also to their economical effectiveness coming from the use of natural bauxite resources. They have already been successfully employed in molten iron torpedo cars, blast furnace troughs and incinerator linings and may still acquire wider applications in high temperature industries. Their mechanical properties at high temperatures is an important factor to consider for such applications. Evaluation of thermo-mechanical properties may provide useful engineering data to estimate the performance of refractory lining under complex state of stress at high service temperature, and may also help to detect possible trends and avenues for further developments with the aim of increasing service life and expanding application areas.

In this paper, high temperature strength and thermal shock of ultra-low cement, bauxite-based SiC-containing castables (hereafter referred to as bauxite–SiC castables) have been investigated and the results are discussed with relation to microstructural features of these materials.

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2. Experimental procedure

2.1. Raw materials

The raw materials used for specimen preparation include:

- Sintered bauxite: $Al_2O_3 \geq 89\%$, $SiO_2 > 5\%$,—aggregates (5–0.088 mm) and fines (<200 mesh, D_{50} = 38.5 μm; <325 mesh, D_{50} = 14.1 μm).
- Silicon carbide-fillers: SiC ≥ 96%, <200 mesh.
- Calcium aluminate cement (Secar 71, Al_2O_3 69.0–72.2%, CaO 27.0–30.0%, D_{50} = 12 μm).
- Microsilica: $SiO_2 \geq 95.0\%$, (<1.5 μm, D_{50} = 0.5 μm).
- Ultra-fine alumina: $Al_2O_3 \geq 98.5\%$, (<4.0 μm, D_{50} = 1.8 μm).

2.2. Formulations of specimens

Andreasen particle size distribution model, with approximate q value of 0.29 was used for the design of particle size composition of the castables. Two series of bauxite–SiC castable specimens have been prepared. Ultra-fine alumina/microsilica (uf-Al_2O_3/SiO_2) ratio is 75:25 for A series and 25:75 for S series; SiC addition varies from 4 to 16% in both series. Their formulation is given in Table 1.

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Table 1
Formulation of bauxite–SiC castable specimens

Code	Sintered bauxite aggregates[a] (%)	Fines (<0.074 mm) (%)		Bonding system		
		Bauxite	SiC	CA	Micro-silica	Ultra-fine Al_2O_3
A series (Al_2O_3/SiO_2 = 75/25 in micropowder)						
A0	65	27	0	2	1.5	4.5
A4	65	23	4	2	1.5	4.5
A8	65	19	8	2	1.5	4.5
A12	65	15	12	2	1.5	4.5
A16	65	11	16	2	1.5	4.5
S series (Al_2O_3/SiO_2 = 25/75 in micropowder)						
S0	65	27	0	2	4.5	1.5
S4	65	23	4	2	4.5	1.5
S8	65	19	8	2	4.5	1.5
S12	65	15	12	2	4.5	1.5
S16	65	11	16	2	4.5	1.5

[a] Aggregate: 5–0.074 mm.

2.3. Specimen preparation

The raw materials are uniformly mixed with 5.4% water addition and cast to produce specimens of 160 mm × 40 mm × 40 mm or 125 mm × 25 mm × 25 mm size. After curing and drying, the specimens are heat treated at 1400 °C for 3 h in reducing atmosphere. After firing their porosity was in the range of 13–18% and cold modulus of rupture was in the range of 5–17 MPa, indicating the specimens were fairly well sintered.

2.4. Test methods

Three point bending method was employed to measure the hot modulus of rupture (HMOR) at 1300 and 1400 °C for the specimens of A and S series; to assess the modulus of rupture–temperature relationship at temperatures up to 1400 °C for specimens A8 and S8; and to study the stress–strain relationship in the specimen S8, loaded up to 500 N at different test temperatures.

To evaluate the thermal shock resistance of castables, residual strength ratio was determined after one thermal shock cycling from 1200 °C to room temperature (ΔT = 1200 °C) for ten specimens (A series and S series). Also, critical temperature difference (ΔT_c) was determined from residual strength—ΔT curves at ΔT from 400 to 1300 °C for two specimens (A8 and S8).

The specimen size for all the above tests was 160 mm × 40 mm × 40 mm, except for stress–strain tests (125 mm × 25 mm × 25 mm).

3. Results and discussion

3.1. High temperature strength properties of bauxite–SiC castables

3.1.1. HMOR

The hot modulus of rupture values of specimens tested at 1300 and 1400 °C in reducing atmosphere of fired bauxite–SiC castable specimens are shown in Fig. 1.

From Fig. 1, it can be seen that:

(1) HMOR values of S series specimens (ultra-fine Al_2O_3/SiO_2 = 25/75) at 1300 °C are higher than those of A series specimens (ultra-fine Al_2O_3/SiO_2 = 75/25) at all levels of SiC addition.
(2) For A series specimens, HMOR at 1300 °C tends to increase with the increase of SiC content from 4 to 16%. In a specimen with 16% SiC addition, HMOR reaches 6.6 MPa which is 5.5 times higher than that of specimen without SiC (1.2 MPa).
(3) For S series specimens, there is a significant increase in HMOR at 1300 and 1400 °C when 4 or 8% SiC is added. With further SiC addition, HMOR tends to decrease back to the values for SiC-free castables. Increase of testing temperature from 1300 to 1400 °C leads to considerable decrease of HMOR values.

The above results may be interpreted in terms of microstructure of the castables: (1) the mineral phases of bauxite castable specimens are essentially corundum, mullite, and glass. Their microstructure is mainly composed of granular

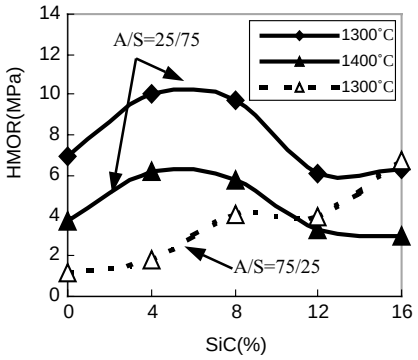

Fig. 1. Variation of HMOR of bauxite–SiC castables at 1300 and 1400 °C with SiC content.

corundum skeleton structure interlaced with mullite crystals. The amount of microsilica added in specimen S0 is 3% higher than that of specimen A0, which means the mullite content in S0 is approximately 11% higher than in A0. This significant increase in mullite content contributes to the higher HMOR of S castables. (2) For A series specimens, when SiC is added, the prismatic SiC crystals are integrated into the skeleton structure of granular corundum together with small amount of mullite crystals which leads to a reinforcing effect. This explains the substantial increase of HMOR with increase of SiC addition in A series. (3) For S series specimens, the granular corundum skeleton structure is partially filled with mullite crystals; when 4–8% SiC is added, the SiC crystals would be incorporated in the skeleton structure (see Fig. 2), creating a reinforcing effect. However, when 12–16% SiC is added, the excess of SiC crystals may disrupt the skeleton structure to some extent, weakening the structure.

3.1.2. MOR–T curves

Two specimens containing 8% SiC addition (A8 and S8) were selected in order to investigate the changes in MOR with temperature. The curves obtained are shown in Fig. 3.

The results show that in the low temperature range (20–600 °C), there is only a slight increase of MOR with an increase in temperature. In the medium temperature range (800–1000 °C), MOR of specimens increases significantly, reaching a maximum at 800 °C (specimen A8) and 1000 °C (specimen S8), followed by a decrease in strength at higher temperatures.

Zhong [1] suggested that MOR–*T* curves of refractory materials may be classified into two types. In type I materials, strength increases with temperature up to an inflexion point (T_m), after which strength decreases with temperature. In type II materials, the strength remains roughly the same at low and medium temperatures, but at a certain point, strength begins to decrease with temperature. In general, materials with two or more crystalline phases belong to type I, whereas materials containing single crystalline phase belong to the type II.

It is clear that the above MOR–*T* curves in Fig. 3 belong to type I. The increase of strength with temperature rise at low and medium temperatures may be attributed to thermal expansion mismatch of the major crystal phases (coefficient of thermal expansion for corundum, mullite and SiC is 8.0–8.5, 5.0 and 4.7 × 10^{-6} °C^{-1}, respectively). The rapid decrease of strength from 1200 to 1400 °C is mainly due to the softening of glassy matrix.

3.1.3. Stress–strain relationship

Specimen S8 (size 125 mm × 25 mm × 25 mm) is selected for investigating stress–strain behavior from RT to 1200 °C. The stress–strain curves obtained are shown in Figs. 4 and 5.

From Figs. 4 and 5, the stress–strain behavior may be divided into three stages: (1) elastic range (RT–600 °C): the stress–strain relationship is a reversible straight line; only very slight decrease in deformation is observed; (2) "plastic flow range" (800–1000 °C): the stress–strain curves exhibit a permanent deformation; (3) "viscous flow" range (1000 °C and above): there is prominent strain increase with increase of stress, indicating viscous flow due to softening of the glassy matrix [2,3].

According to Zhong et al. [4], thermo-mechanical behavior of sintered bauxite refractories is determined largely by microstructural characteristics and depends on two principal factors: (1) the amount and viscosity of the glassy matrix

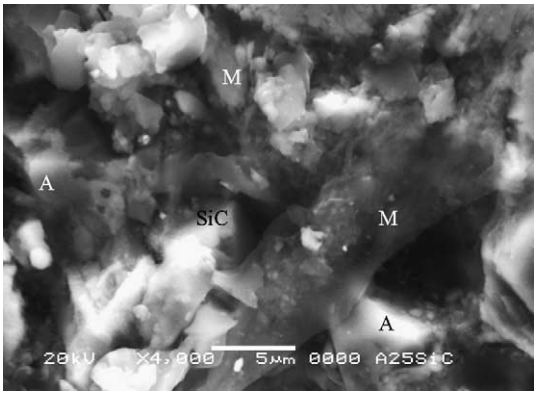

Fig. 2. SEM photograph of bauxite–SiC specimen (S8); A, alumina; M, mullite crystals.

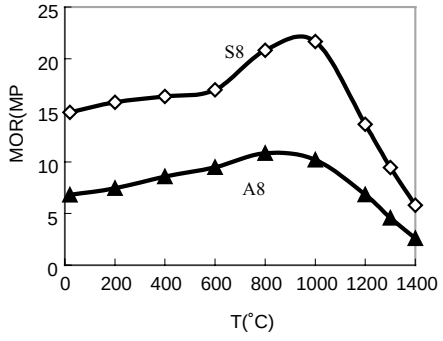

Fig. 3. MOR–*T* curves for specimens A8 and S8.

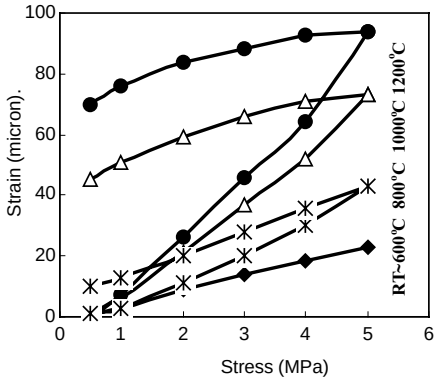

Fig. 4. Stress–strain curves of specimen S8.

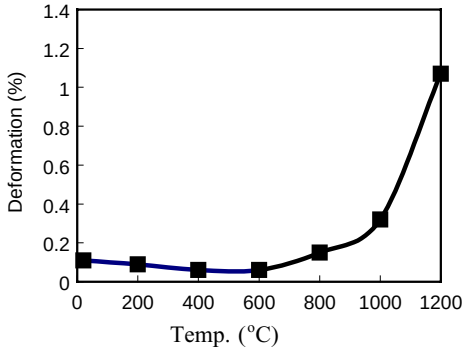

Fig. 5. Variation of deformation with temperature for specimen S8 under 500 N load.

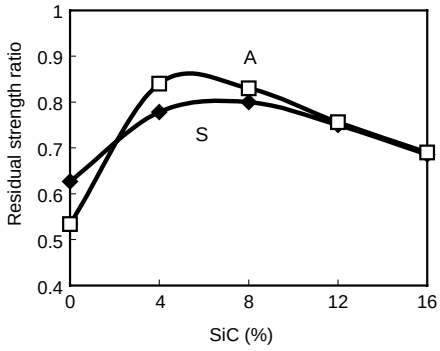

Fig. 6. Variation of residual strength ratio (σ_R/σ_f) with SiC addition ($\Delta T = 1200\,^{\circ}C$) for bauxite–SiC castable specimens (A and S series).

(glass effect); (2) the extent and mode of crystal-to-crystal bonding (crystal effect).

In this work, in the low temperature range prior to incipient plasticity (up to 600 °C), the accumulated strain depends mainly on the rigidity of the individual corundum, mullite and SiC crystals, and also on their degree and mode of bonding. At this stage, glass effect could only play an insignificant role, if any at all. In the plastic flow range, both crystal effect and glass effect would simultaneously exert their influence, but the controlling factor is the crystal effect. In the viscous flow range (temperatures 1000 °C and above), the glass effect becomes the dominant factor: the glassy matrix tends to soften resulting in substantial deformation under stress.

3.2. Thermal shock resistance (TSR)

3.2.1. Residual strength ratio at $\Delta T = 1200\,^{\circ}C$

In TSR tests, the specimens are heated to a predetermined temperature (T) and then quenched in running water (T_w). After drying, the residual rupture strength in bending (σ_R) is measured and compared with the original strength (σ_f). Residual strength ratio (σ_R/σ_f) at temperature difference $\Delta T = T - T_w$ is a criterion for evaluating TSR.

Residual rupture strength ratio at $\Delta T = 1200\,^{\circ}C$ of the two series of sintered bauxite–SiC castable specimens (series A and S) are determined by measuring MOR before and after the thermal shock cycling. The results shown in Fig. 6 clearly demonstrate that compared with the specimens without SiC, the residual strength ratio of SiC-containing specimens is considerably increased, and it also tends to increase with SiC addition. The maximum strength is attained in castables with 4–8% SiC.

3.2.2. Critical temperature difference (ΔT_c)

Two specimens with 8% SiC (A8 and S8) were selected for determining the changes in MOR after thermal shock for ΔT in the range from 400 to 1300 °C. As seen from Fig. 7, there was no change in strength for both specimens up to 800 °C, but at higher temperatures the strength decreased considerably. It is concluded that the critical temperature difference (ΔT_c) for both specimens is approximately 800 °C. According to Hasselman theory [5], ΔT_c indicates the ability of material to withstand abrupt temperature variations. In the present case, when ΔT is 400–800 °C, the interior part of specimens is not affected by thermal shock and remains intact. But when ΔT is in the range of 800–1300 °C, the inside part of the specimen is affected by thermal shock as the high thermal stresses generated in the material would extend original cracks and initiate formation of new cracks.

The improvement of TSR of bauxite–SiC specimens by SiC addition may be due to higher thermal conductivity, lower thermal expansion and higher strength of SiC, as well as to the presence of prismatic or elongated crystals in the microstructure of castables. Incorporation of those crystals in the corundum–mullite matrix produces a reinforced but flexible structure, which leads to increase in the hot strength, as well as the spalling resistance.

4. Conclusions

(1) SiC addition in ULC bauxite-based castable specimens has significant effect in improving HMOR at 1400 °C. For A series specimens (ultra-fine Al_2O_3/SiO_2 = 75/25), HMOR increases with increase of SiC content, whereas for S series specimens

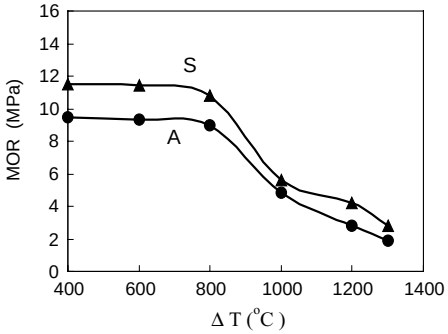

Fig. 7. Residual strength of castables A8 and S8.

(ultra-fine $Al_2O_3/SiO_2 = 25/75$), the optimum SiC addition is 4–8%.

(2) MOR–*T* curves illustrate that MOR increases with temperature up to inflexion point at 800 or 1000 °C, after which MOR decreases significantly.

(3) The stress–strain behavior of the specimens may be divided into three stages: elastic range from RT to 600 °C; "plastic flow range" (600–1000 °C) and " viscous flow" range (1000 °C and above).

(4) SiC addition is also very effective in improving TSR of castable specimens. With increase of SiC contents, significant increase in residual strength ratio is observed, with maximum values at 4–8% SiC addition.

(5) The positive effects of SiC addition on HMOR and TSR of bauxite-based castables may be attributed to: (a) low thermal expansion, high thermal conductivity and high strength of silicon carbide phase; (b) reinforcing effect of SiC crystals integrated into corundum–mullite.

Acknowledgements

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