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RESEARCH

Parameters influencing the characteristics of the nano-bonded aluminosilicate based refractory castables

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Abstract

Replacing calcium aluminate cement as hydraulic binder by silica sol as sol-gel binder for refractory castables is known to reduce drawbacks of hydraulic binders but still comprehensive information regarding the effect of various raw materials and additives are required. In this research bauxite, andalusite and argellite were chosen as aluminosilicate aggregates and silica sol as binder and the effect of citric acid, micro silica and cement as setting agent were investigated for different compositions. Mechanical strength of the obtained castables at different temperatures of 110, 1000 and 1400°C were probed for various compositions. Finally based on the maximum mechanical strength of 342.5 and 241 Kg/cm^2 at 110°C, workability and flowability of the castables, optimum compositions were selected. The used amounts of citric acid, micro silica and cement for bauxite optimized composition were 0.04%, 2% and 1% while there were 0.02%, 0% and 1%, respectively for andalusite based one. The effect of sol-gel binder on the corrosion resistance of the optimized compositions was investigated in contact with molten sodium silicate using static cup test. Bauxite based castables showed mechanical strength higher than andalusite ones, while the later exhibited better corrosion resistance which related to the intrinsic characteristics of the used aggregates.

Keywords Silica sol · Refractory castable · Nano bond · Bauxite · Andalusite · Corrosion resistance

Introduction

Refractory castables as a main group of monolithic refractory family have found growing demand due to the vast requirements of industrial operations in iron and steel making, cement and glass production, petrochemical and etc [1, 2]. Compared to shaped refractories (bricks), castables are most popular in harsh environments owing to easier and cheap installation and better performance [3, 4]. Castables composition is usually comprised of different refractory aggregates, bonding agents, fillers and additives. The castable skeleton is composed of aggregates filled by finer particles of filler (such as fumed silica or fine alumina) which is responsible for flow and rheology properties. The bonding agent or binder is responsible for holding the whole structure. Binders are classified as hydraulic, coagulation, chemical and sol-gel [2, 5]. Dispersants are specific charged molecules used to fulfill the efficient dispersion and reduce water demand and provide good flow through electrostatic or electrosteric mechanisms [6].

Calcium aluminate cement as common hydraulic binder leads to outstanding properties but some drawbacks appear which give rise to shift from regular cement towards low cement, ultra-low cement and finally non-cement castables [7–9]. The presence of CaO in the cement leads to the creation of low melting phases such as CAS_2 ($CaO.Al_2O_3.2SiO_2$) and C_2AS ($2CaO.Al_2O_3.SiO_2$) which deteriorates refractory parameters [10–12]. Furthermore noticeable drop of strength at intermediate temperatures happens due to the decomposition of hydrated products [13].

Sol-gel bonding system in refractory castables is conducted by mixing precursor solution containing solid particles in nano size and a solvent. Then sol is transformed into gel by evaporation of solvent or adding chemical agent which aids crosslinking of the particles to form 3-dimensional network. This 3-dimensional network formation is

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called gelation and this gel can act the role of binder in non-cement castables [7, 12]. Gel formation inhibits the generation of hydrated phases and subsequent risk of explosive spalling of castables and also cracking during drying [13, 14]. The 3-D polymeric network unifies refractory aggregates and consolidates them during green strength and then it is substituted by ceramic bonding after sintering [5]. Various sols such as alumina, silica, mullite, spinel and boehmite sols have been investigated to be used as colloidal binders in refractory castables but among all silica sol is commercially and widely exploited [12, 15–16]. Silica sol is kind of stable colloidal binder composed of dispersed spherical amorphous silica nano particles in water [17]. Application of Silica sol as binder has advantages like less or no water addition, short mixing time, fast drying and sustainable green strength [13, 17]. Also silica sol binder can overcome all other rivals in the category of binders due to its cheap price, extended shelf life and good volumetric stability at high temperatures [5, 13]. Fast and easy drying of colloidal binders in comparison to hydraulic ones relies on the humidity requirement for cement based castables in the initial drying step for strength development [12]. Besides, the nano-sized particles of silica participate in the in-situ mullite formation after sintering in castables containing alumina [18]. The presence of mullite phase itself helps to improve refractoriness, thermal and chemical stability of the refractory [17]. The gelation mechanism is based on the formation of siloxane groups (Si-O-Si) at the expense of silanol groups (Si-OH) according to the reaction below [12, 19–20] and Fig. 1. Silanol groups exist as cover layer on the surface of silica sol particles. By removing water molecules during drying process siloxane bonds are formed and entrap solid aggregates as illustrated in Fig. 1-d [2, 5].

$$-Si-OH+OH-Si-\rightarrow -Si-O-Si-\ +H_2O \qquad (1)$$

The significant matter about colloidal binder is the low green strength of the refractory castables containing silica sol which requires further efforts to get improved. Low green mechanical strength causes difficulties while demolding and transportation specially in large blocks such as electric arc furnace roof [13–14, 21]. Therefore many researchers are investigating methods and parameters increasing green strength of silica sol bonded refractory castables. One of the approaches to achieve this purpose is using setting agents which spoil proper workability and flowability [21]. Thus optimized amounts of agents (such as cement, MgO, CaO, $CaCl_2$, etc.) must be used to compromise both mechanical properties and concrete workability [22].

The main object of this work is to improve and optimize the mechanical strength of the silica sol bonded castables by using various amounts of parameters such as microsilica, cement and citric acid for bauxite and andalusite based refractory castables. The effect of microsilica, cement and citric acid addition on cold crushing strength (CCS) were evaluated at different temperatures of 110, 1000 and 1400°C. The corrosion behavior of the nano-bond refractory castables in contact with molten silicate at 1400°C was also investigated.

Materials and methods

China bauxite (China Mineral Processing LTD), andalusite, argelite aggregates (supplied by Iranian mines), alumina fines (325 mesh), microsilica (Elkem), cement 70 (Amol carborundom company), citric acid and Silica sol were employed as raw materials. The chemical composition of the raw materials determined by XRF (X-ray fluorescence analysis, SPECTRO XEPOS spectrometer) are summarized in Table 1. Silica sol with particle concentration of 40%, particle size of 10–30 nm and pH = 9–10 was used. The aforementioned raw materials were mixed together according to the formulations given in Tables 2 and 3. After mixing the prepared raw materials with water, samples were cast into 50×50×50 mm^3 metal mold specimens. After demolding, the samples were cured at room temperature and 110°C for 24 h respectively and then fired at 1000 and 1400°C for 3 hours. Cold crushing strength (CCS) of the castables were measured after drying and firing at three

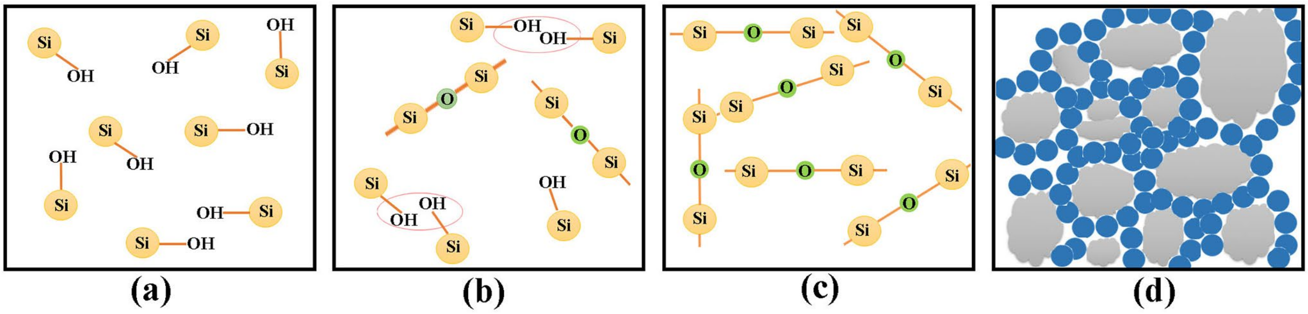

Fig. 1 Different steps of gelation mechanism of silica-sol, (**a**) silica sol, (**b**) drying step, (**c**) after drying and (**d**) 3-D network encapsulated aggregates

Table 1 The chemical composition and physical property of the used raw materials

Raw material	Al_2O_3(%)	SiO_2(%)	TiO_2(%)	Fe_2O_3(%)	CaO(%)	MgO(%)	Na_2O(%)	K_2O(%)	P_2O_5(%)	Porosity
China bauxite	86	7.4	3.4	1.8	0.44	0.2	0.13	0.22	0.12	7%
Andalusite	58.74	38.75	0.1	0.91	0.09	0.18	0.14	0.26	0.06	2.45%
Argelite	58.64	34.66	2.56	3.06	0.18	0.34	0.06	0.36	0.061	10.35%
Fine alumina	99.2	< 0.06	0.01	0.02	0.02	0.01	0.32	0.02	0.01	-
Microsilica	1.13	87.82	0.03	3.17	0.5	1.04	0.78	0.93	0.19	-
Cement 70	69.5	0.4	0.4	0.24	28.3	0.24	0.2	0.3	0.17	-

Table 2 Chemical compositions of the prepared andalusite based castables

Raw material	A1	A2	A3	A4	A5	A6	A7	A8	A9
Argellite 3–5	17	17	17	17	17	17	17	17	17
Andalusite 1–3	26	26	26	26	26	26	26	26	26
Andalusite 0–1	22	22	22	22	22	22	22	22	22
Andalusite 200	24	24	24	25	24	23	24	23	22
Alumina fine	10	10	10	10	10	10	10	10	10
Microsilica	0	0	0	0	0	0	0	1	2
Cement 70	1	1	1	0	1	2	1	1	1
Silica sol	7	7	7	7	7	7	7	7	7
Citric acid	0	0.02	0.04	0.02	0.02	0.02	0.02	0.02	0.02

Table 3 Chemical compositions of the prepared bauxite based castables

Raw material	B1	B2	B3	B4	B5	B6	B7	B8	B9
Bauxite 3–5	26	26	26	26	26	26	26	26	26
Bauxite 1–3	17	17	17	17	17	17	17	17	17
Bauxite 0–1	22	22	22	22	22	22	22	22	22
Bauxite 325	22	22	22	23	22	21	24	22	20
Alumina fine	10	10	10	10	10	10	10	10	10
Microsilica	2	2	2	2	2	2	0	2	4
Cement 70	1	1	1	0	1	2	1	1	1
Silica sol	7	7	7	7	7	7	7	7	7
Citric acid	0.02	0.04	0.08	0.04	0.04	0.04	0.04	0.04	0.04

different temperatures of 110, 1000 and 1400°C. Cold crushing strength (CCS) was quantified based on ASTM C133-97 using Azemoun CE280 testing equipment. For each composition two samples were prepared and the average value is reported. In order to analyze the formed phases in the samples, X-ray diffractometer (XRD) using Philips pw1730 in 2θ range of 10–70° with Cukα radiation at $\lambda = 1.5418$°A was conducted.

Static cup test was used in order to examine the corrosion resistivity of the refractory castables. For this purpose the central hole of each prepared cylinder crucible was filled with 90 g of melt composition powder (50% silica sand + 50% soda ash). The crucible then fired at 1400°C for about 24 h in air atmosphere. After that the samples were cooled down and were cut along the center. Corrosion resistance and melt infiltration were investigated through the images taken by field emission scattering electron (FESEM, MIRA TESCAN).

Results and discussions

The measured mechanical strength (CCS) at different temperatures of 110, 1000 and 1400°C for the bauxite and andalusite based samples are depicted in the diagrams shown in Figs. 2, 3 and 4. The effect of three different parameters of citric acid, cement and microsilica content on CCS were evaluated.

As it is visible in Fig. 2 increasing acid concentration for bauxite sample from 0.02 to 0.04% leads to enhancement in the CCS (at 110°C), but increasing more than optimum amount (0.08%) makes reverse result. However at higher temperatures the trend is different from 110°C, but green mechanical strength is much more important due to demolding and transportation. Therefore green mechanical strength is considered as evaluation criterion. Moreover, increasing acid more than 0.04% showed negative effect on the casting's setting and workability. Short time of setting leads to the weak workability of the castable. Castable with 0.08% acid showed shorter setting time which causes less workability of the castable. So increasing acid more than optimum

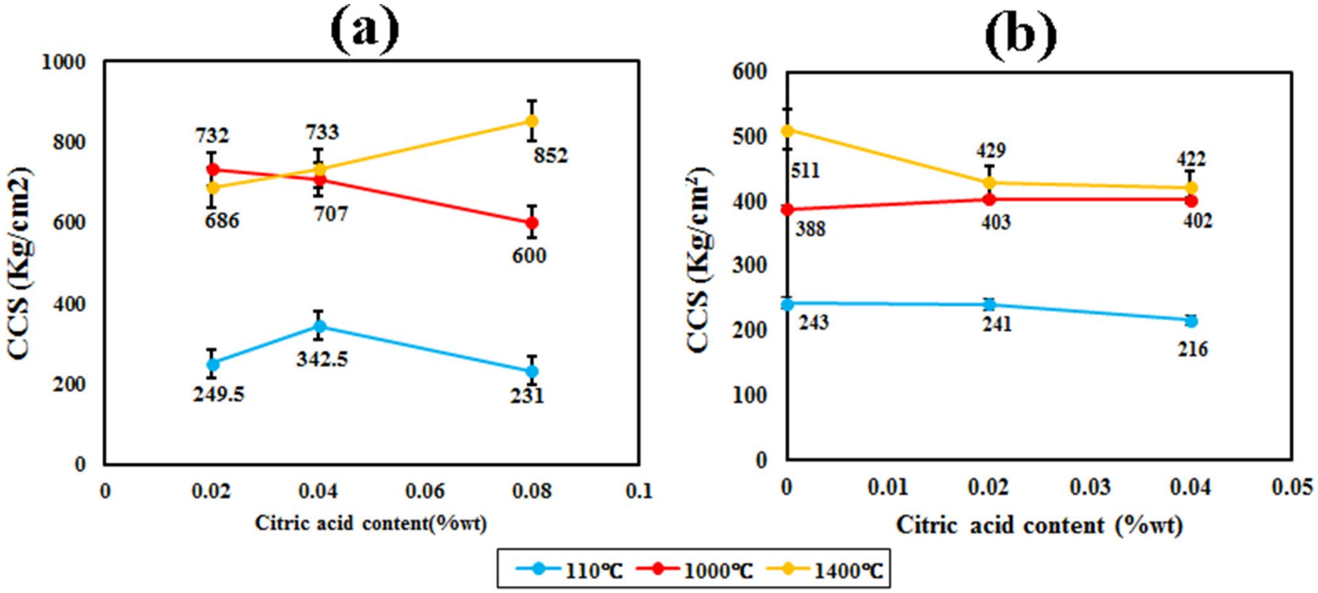

Fig. 2 CCS values as function of citric acid content for (**a**) bauxite and (**b**) andalusite based castables cured at different temperatures

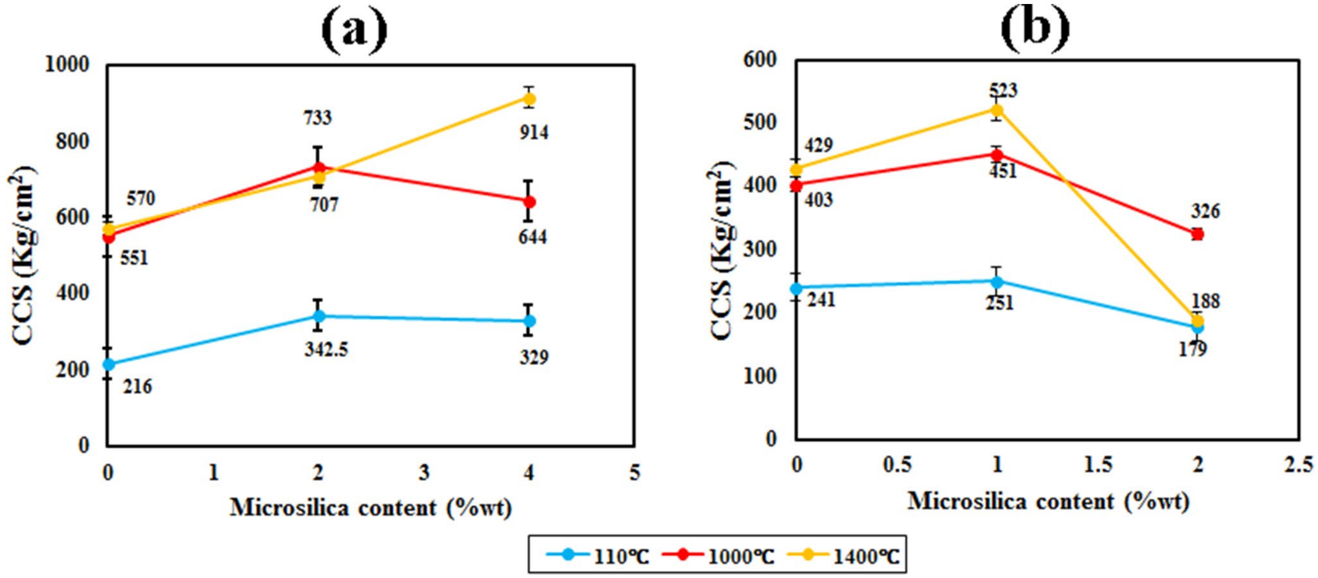

Fig. 3 CCS values as function of microsilica content for (**a**) bauxite and (**b**) andalusite based castables cured at different temperatures

amount has negative effect both on mechanical strength and workability. In the case of andalusite based samples, increasing acid more than optimum value of 0.02% leads to drop in CCS value. For sample without acid and with 0.02% the mechanical strength is almost same but workability and setting time is different. Sample without acid shows longer setting time which is not suitable. Acid amount of 0.04% presents so much lower setting time, while sample with 0.02% shows suitable workability and mechanical strength simultaneously.

Dispersants are used in refractory castables to prevent close approximation of particles through the steric or electrical double layer formation on the surface of particles. Attractive van der Waals forces among the particles are overcome by sufficient thickness of these layers. Excessive increase of these layers also must be avoided as can lead to the entrapment of water around the particles and the reduction of castable flowability. Due to high solid loading in refractory castables and short interparticle distances, short chain molecules are capable to provide adequate electrical double layer to prohibit particle coagulation. According to the literature, citric acid as a dispersant adsorbs preferentially on alumina surface at acidic pH values and low adsorption efficiency happens at basic pH values [23]. In the case of

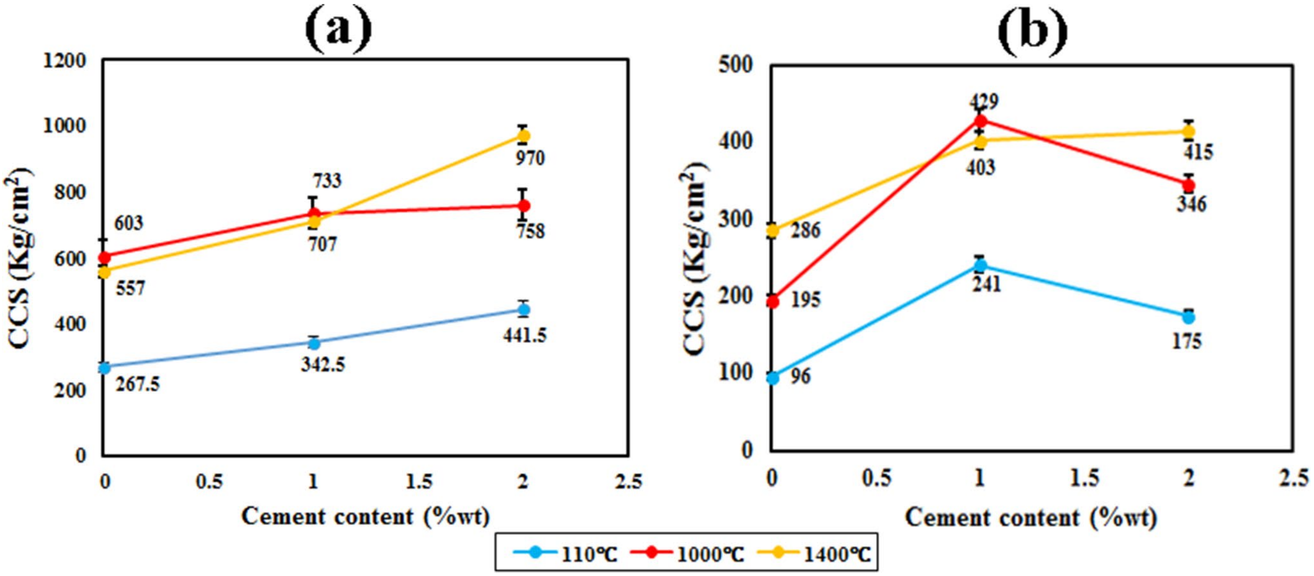

Fig. 4 CCS values as function of cement content for (**a**) bauxite and (**b**) andalusite based castables cured at different temperatures

bauxite based castables due to lower amount of SiO_2 in the composition and low acidity, adsorption efficiency of citric acid gets low and more acid is needed to saturate particles surface. Therefore the composition with 0.04% citric acid can be chosen as optimum sample. Lower amounts of acid (0.02%) cannot be adequate to cover the particles and for amounts more than 0.04% leads to the reduction of concrete flow. As it is seen for andalusite based castable the optimum sample is achieved at citric acid of 0.02% without microsilica. Based on the higher amount of SiO_2 in andalusite composition and higher acidity, citric acid adsorbed efficiently and low acid value meets this condition. In the presence of microsilica in the composition acidity enhances much more and thus 0.02% acid is more than required amount and then causes the drop in the flowability.

Microsilica as filler fills the voids initially occupied by water and water addition decreases and flowability improves. So in the absence of microsilica voids are filled by water so the water consumption is increased [13]. By increasing microsilica up to limited amount in both bauxite and andalusite castables in Fig. 3, mechanical strength enhances and excessive addition (more than optimum amount) of microsilica leads to reduction in strength arises from bad workability at room temperature. Moreover by the addition of microsilica the setting time of castable was decreased. For the amounts more than optimum level the setting time was so short which makes workability reduction.

Improvement of strength by microsilica addition is attributed to the more chemical Si-O-Si bonds formations by the presence of microsilica and colloidal silica together. Increasing activated SiO_2 in the composition leads to increasing of chemical bond and improvement of the strength [24]. As it is seen after heat treatment at higher temperatures, much more increase of strength occurred in comparison to dried samples. So in-situ mullite formation by the reaction of microsilica by alumina can be accounted as a reason. Microsilica more than optimum amounts lead to strength reduction both at high and low temperatures. The reason can be ascribed to the liquid phase formation at high temperature treatments [24]. Improving mechanical strength by sintering can be explained by mullite formation through the reaction between alumina and silica particles. In the case of cement bonded castables liquid phase formation at high sintering temperatures leads to strength reduction. Low melting phases starts attacking mullite bond and leads total strength reduction.

In silica sol bonded samples by water removal and reduction of inter particle distance, siloxane bonds are formed as showed in Fig. 1. Ca^{2+} and Al^{3+} ions produced by cement dissolution can play a role of gelling agents and promote gelation mechanism. Net repulsion among nanosilica particles decreases due to the inference of these mentioned ions. The formed three-dimensional network encapsulates refractory aggregates results in strength enhancement of the castable. Optimum amounts of cement should be considered, as excess amounts ruins both fluidity and workability of the castable. Silica sol and cement reaction generates crystalline phase of stralingite ($CaO.Al_2O_3.SiO_2.H_2O$) according to the literature which assists attaining maximum strength accompanying gelling mechanism [11]. At lower curing temperature hydrated phases also help to ameliorate mechanical strength.

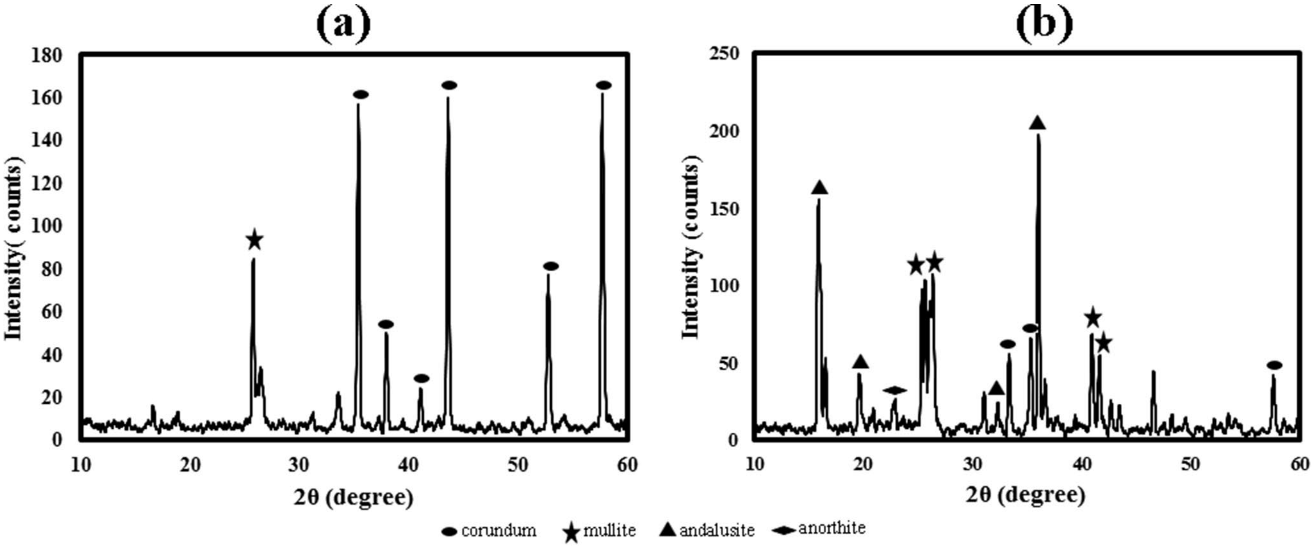

Fig. 5 The XRD pattern of the (**a**) bauxite and (**b**) andalusite based samples

Furthermore, extra amounts of cement consume extra water which creates cracks while drying and increases porosity. So optimum content should be chosen which can balance all required characteristics such as flowability, workability, mechanical strength and cracking. For both samples 1% cement was optimum to keep both flowability and strength at suitable level (Fig. 4).

As mentioned earlier mullite formation through the reaction between alumina and silica particles leads to the improvement of mechanical strength. So this claim is proved by the XRD patterns shown is Fig. 5. As it is depicted for bauxite based sample mullite and corundum peaks are visible while for andalusite based one, andalsuite, mullite, corundum and anorthite ($CaAl_2Si_2O_8$) phases appeared. Anorthite phase also generated by the reaction between cement and alumina and silica particles.

The corrosion behavior of the prepared cement bonded and sol-gel bonded castables in contact with corrosive media melt was evaluated. The vertical cut cross-sections of the corroded castables are shown in Fig. 6.

As it is evident from the photographs of the corroded samples liquid melt was infiltrated in the refractory material and the penetration and corroded area is shown with red arrows. As it is seen andalusite based castable shows pure and unaffected interface between castable and molten, while bauxite based sample exhibits severe corrosion. As seen changing hydraulic binder to sol gel one does not make much difference in the corrosion resistance behavior. In the andalusite based one due to less porous structure, there is limitations for molten infiltration into the refractory material. The interface between refractory material and molten is specific and separate. The FESEM images after corrosion is shown in Fig. 7. The microstructure of the castable at the interface is composed of aggregates and there is no sign of molten over the aggregates. This indicates the absence of molten infiltration into the andalusite refractory castable. For bauxite sample, the microstructural variations are depicted in FESEM images shown in Fig. 8. At the interface the whole castable microstructure is covered by melt which is owing to the porous nature of bauxite and easy molten infiltration. This shows molten infiltration into refractory through pores by capillary or wetting mechanisms.

LCC castable contains 7% cement as binder requires some higher amounts of water and this leads to high porosity and vulnerable to melt infiltration. Less water was consumed in the preparation of sol-gel bonded samples leading to less apparent porosity after drying and sintering and subsequently more corrosion resistance in comparison to cement contained sample.

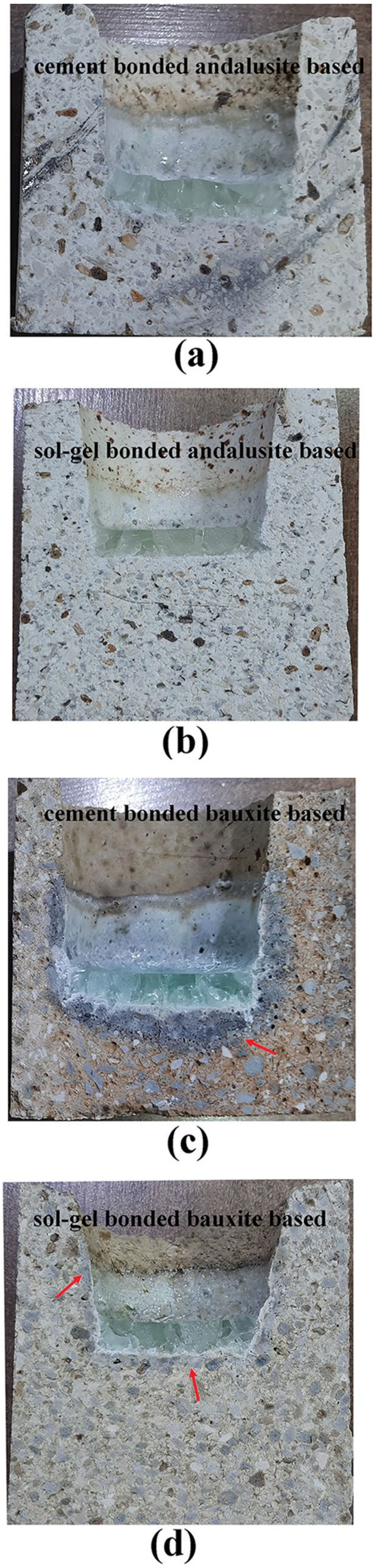

Fig. 6 Cross-section photographs of the refractory castables filled by molten after corrosion cup test

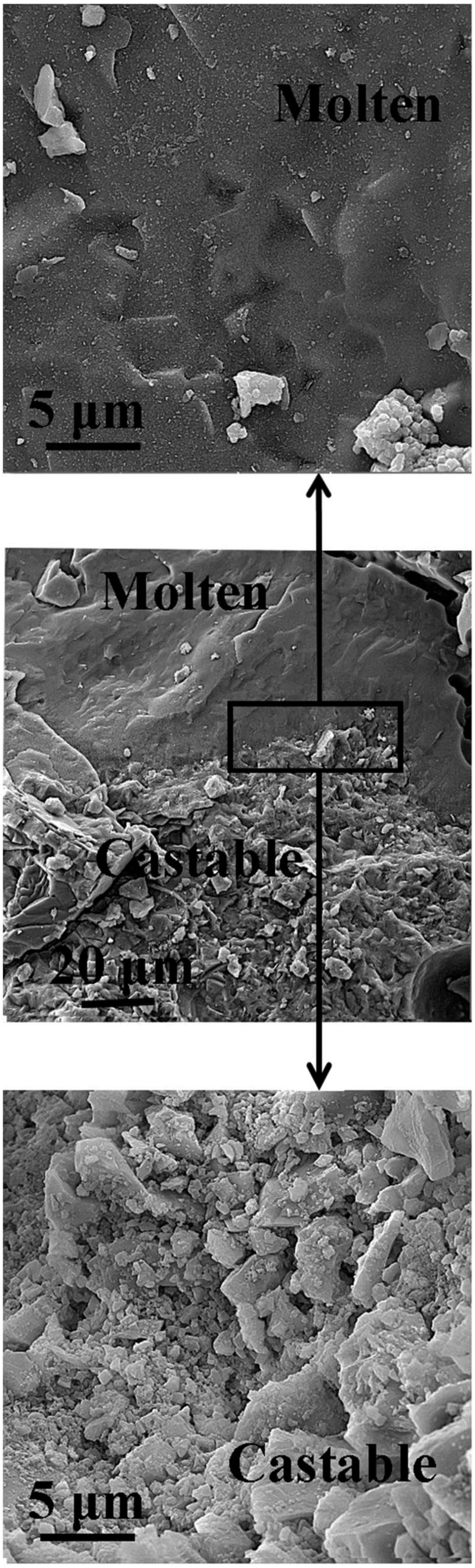

Fig. 7 FESEM images of the andalusite based refractory brick in contact with molten after corrosion test

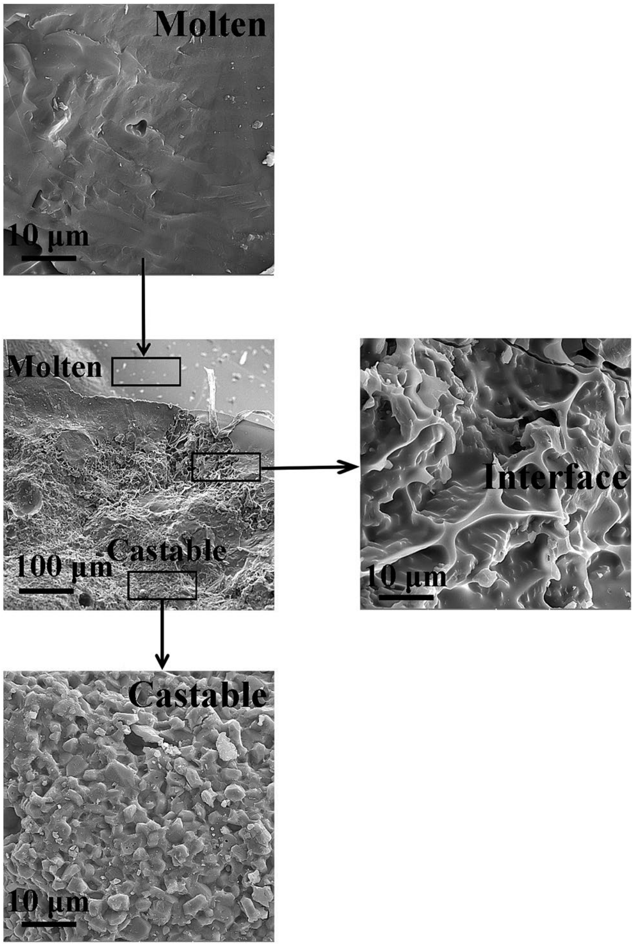

Fig. 8 FESEM images of the bauxite based refractory castable in contact with molten after corrosion test

Conclusion

In this research work, the role of micro silica, cement and citric acid addition and temperature (110, 1000 and 1400°C) on the properties of sol-gel bonded bauxite and andalusite based castables were investigated. According to the maximum CCS values of 342.5 and 251 Kg/cm^2 at 110°C for bauxite and andalusite based castables, the optimized compositions were attained. Bauxite based sample with 1% cement, 2% microsilica and 0.04% citric acid and andalusite based with 1% cement, 0% microsiluca and 0.02% citric acid were selected as optimized compositions. The andalusite based sample showed better corrosion resistance against molten silicate due to its low porosity.

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Declarations

Conflict of interest We declare that we have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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