Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of the European Ceramic Society 24 (2004) 3833–3839

www.elsevier.com/locate/jeurceramsoc

Partial substitution of feldspar by B.F. slag in triaxial porcelain: Phase and microstructural evolution

Kausik Dana, Swapan Kumar Das*

Central Glass and Ceramic Research Institute, Kolkata 700 032, India

Received 16 November 2003; received in revised form 5 February 2004; accepted 21 February 2004

Available online 8 May 2004

Abstract

Feldspar was gradually substituted by B.F. slag (a glassy by-product of Indian steel plant) to the extent of 5–20 mass% in a triaxial porcelain composition consisting of 45 mass% kaolinitic clay, 30 mass% feldspar, 25 mass% quartz. The green compacts were heated at 1200 °C for a period of 120 min. The microstructure and phase changes as they evolve on heating were studied using SEM and XRD techniques. The results reveal that quartz level was reduced from 26 to 9 mass% by the addition of 5% slag, while mullite level was reduced from 20 to 2 mass% by the addition of 10% slag. Beyond this, further addition of slag did not alter the quartz and mullite level much. Slag used in this study was enriched with alumina and contributed towards development of anorthite ($CaO{\cdot}Al_2O_3{\cdot}2SiO_2$) phase by crystallization of melted glassy phase and its quantity increased with increase in slag content. Sudden increase in flexural strength of 20% slag containing body is attributed to stronger pre-stress caused by the difference in thermal expansion coefficient between glassy matrix, quartz and anorthite during cooling process. This also caused circumferential cracking around quartz grains. The paper further discusses the variation in their physico-mechanical characteristics with respect to slag content.

Keywords: Porcelain; Slag; Microstructure; Anorthite; Waste materials

1. Introduction

The phase transformation and microstructure of traditional triaxial porcelain (kaolinite–quartz–feldspar) bodies have been studied in a great detail by many authors.[1–9] In general, porcelain of this kind are heterogeneous with crystalline phases (mainly quartz and mullite) and pores dispersed in a glassy matrix. It is well established that kaolinite on dehydroxylation at around 550 °C give rise to metakaolin which transforms to a spinel-type structure and amorphous free silica at 1000 °C. The spinel transforms to primary mullite and silica at temperatures above 1100 °C. Due to this reaction series, primary mullite is, commonly observed in porcelain microstructure as aggregate of small crystals (<0.5 μm) in the clay relicts. Secondary mullite forms by the reaction of clay relicts with feldspar relicts at around 1200 °C and it appears as a long needle (>1 μm) shaped crystals.[6] Lundin reported that mullite crystals grow from the outer surface of the clay relict into the feldspar relict, suggesting that primary mullite may act as a seed for the nucleation of secondary mullite.[4] The continuous increase in the size of the mullite crystals towards feldspar relict indicates the possible transformation of primary into secondary mullite.[1] At above 1250 °C, silica rich amorphous solution rim forms around quartz grains by dissolution of quartz. Quartz grains start dissolving at 1350 °C and the finer size (<20 μm) almost completely dissolve at 1400 °C resulting a porcelain microstructure consisting of glass and mullite with little quartz. With increasing temperature, the small crystals of primary mullite would be expected to dissolve preferentially, but Schuller[6] reported that only secondary mullite is dissolved partly and the aggregates of scaly primary mullite remain stable at higher temperature. In 1300 °C fired porcelain body cracks often observed in and around large quartz grains due to large thermal expansion mismatch between crystalline quartz and glassy phase in the temperature range of 20–750 °C.[10,11]

Potash feldspar is a commonly used fluxing mineral in standard porcelain bodies. The resources of high grade feldspar minerals have recently began to become depleted.

---

* Corresponding author. Tel.: +91-33-2483-8084; fax: +91-33-2473-0957.

E-mail address: swapan@cgcri.res.in (S.K. Das).

0955-2219/$ – see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2004.02.004

Thus, it is necessary to evolve an alternative source of fluxing materials for porcelain bodies, which can serve to lower the temperature at which the viscous liquid forms. It is widely reported that iron and steel slag is an inexpensive source of alkaline earth oxide used in porcelain system to assist speedier formation of glassy phases.[12–18] Dana and Das[16] observed that metallurgical slags can partly replace feldspar minerals to produce high strength ceramic floor tile bodies with limited and controlled porosity compatible with the firing shrinkage values. Although it is established that glassy material of such kind reacts with other body constituents leading to densification of the body and enhanced the strength, however, the changes in the phase transformation and microstructure are not adequately studied. The main purpose of the present study was to investigate the phase and microstructural changes in standard porcelain body on gradual replacement of feldspar by the B.F. slag. X-ray diffractometry (XRD) and Scanning Electron Microscopy (SEM) techniques were used for phase identification and microstructural study. An attempt was also made to study the variation in their physico-mechanical properties such as linear shrinkage, bulk density, apparent porosity and flexural strength with slag content.

2. Experimental procedure

Five different porcelain samples were prepared as per the batch composition provided in Table 1.

Usual ceramic processing of mixing and wet grinding, drying and powdering, granulation and compaction of samples were followed as adopted in the similar kind of work of the present authors.[18,19] All the compacted samples (60 mm × 14 mm × 5 mm in size) after proper drying (moisture content less than 0.5%) were heated at the temperature of 1200 °C for a soaking period of 120 min in an electrically operated laboratory furnace using on/off control system. A constant heating rate of 8 °C/min was maintained during firing. The fired samples were then subjected to physical tests such as linear shrinkage, apparent porosity and bulk density. Conventional liquid displacement method was followed to measure bulk density and apparent porosity according to Archimedes principle. Flexural strength (three-point bending) of the fired samples was determined by universal testing machine (INSTRON 5500R). The results reported here is the average of six samples.

Table 1
Batch compositions (mass%)

Batches	Kaolinitic clay	Feldspar	Quartz	B.F. slag
NP	45	30	25	0
SP-1	45	25	25	5
SP-2	45	20	25	10
SP-3	45	15	25	15
SP-4	45	10	25	20

Table 2
Chemical analysis of the raw materials

Major chemical constituents (mass%)	Kaolinitic clay	Feldspar	Quartz	B.F. slag
SiO_2	45.41	66.48	98.66	35.35
Al_2O_3	34.39	17.29	0.39	19.15
Fe_2O_3	1.13	0.14	0.07	0.60
TiO_2	0.89	0.02	0.01	0.77
CaO	1.07	0.31	0.10	36.56
MgO	0.76	0.03	0.02	2.99
Na_2O	0.87	2.94	0.09	0.81
K_2O	0.42	11.95	0.12	1.29
MnO	0	0	0	2.09
L.O.I.	14.67	0.71	0.37	0.21

Table 3
Oxide compositions of the experimental bodies

	NP	SP-1	SP-2	SP-3	SP-4
SiO_2/Al_2O_3	3.13	3.04	2.96	2.87	2.78
$K_2O + Na_2O$	5.49	4.80	4.11	3.42	2.74
$CaO + MgO$	1.03	3.14	5.25	7.36	9.47

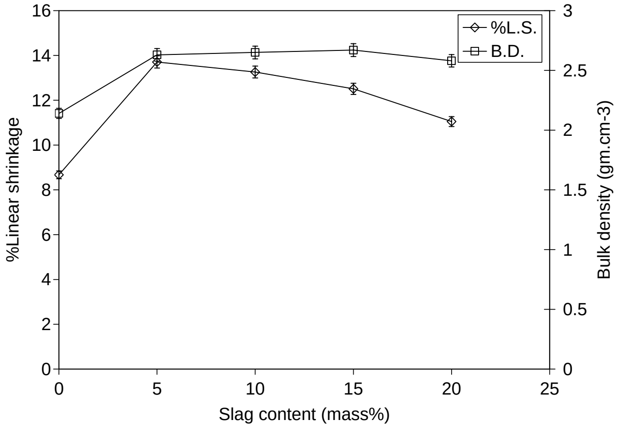


Fig. 1. Variation in linear shrinkage and bulk density with slag content.

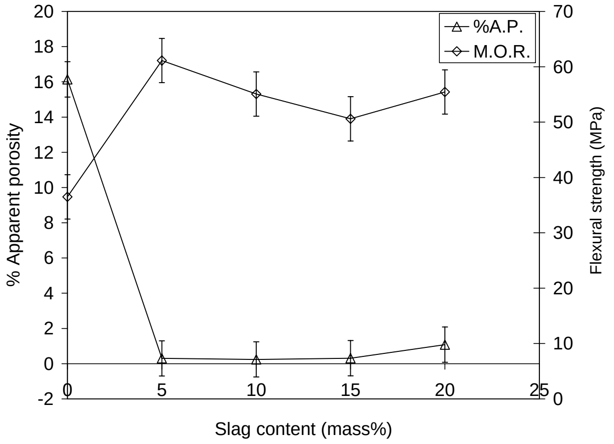


Fig. 2. Variation in apparent porosity and flexural strength with slag content.

X-ray diffraction studies was carried out with powder (−200 mesh BS sieve) of each of the samples. Philips ‘X-Pert Pro’ diffraction unit, attached with secondary monochromator, automatic divergence slit and nickel filter, was used to get monochromatic CuKα radiation. The instrument was run at step scan mode with step size (0.02) and 8 s time per step, within 2θ angle 5° to 75°. The collected data was refined using Profit software. X-Pert plus and Quasor software based on Rietveld were used to calculate the percentage of mullite and quartz, where standard quartz

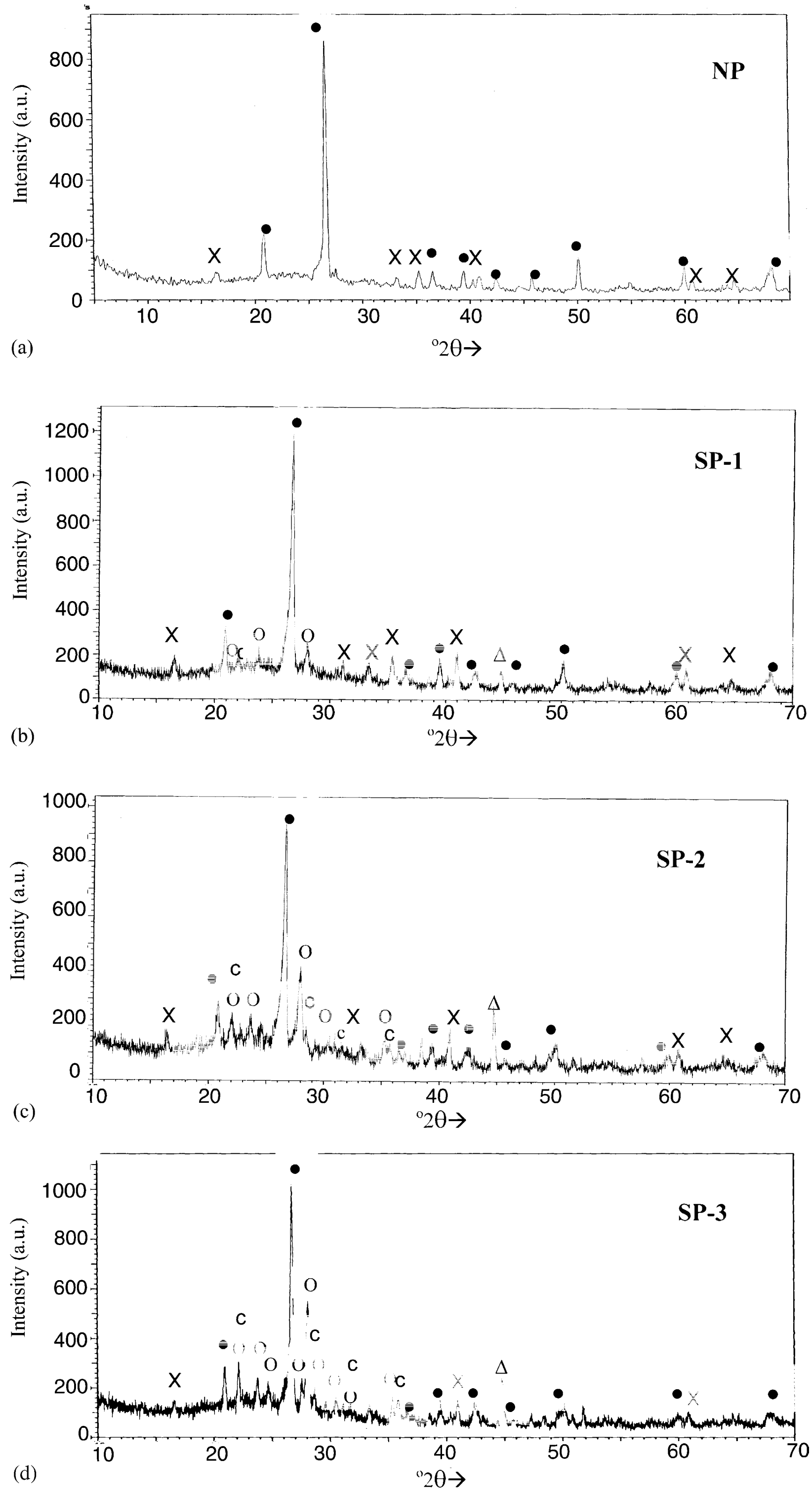


Fig. 3. XRD pattern of 1200 °C heated samples. (a) NP, (b) SP-1, (c) SP-2, (d) SP-3, (e) SP-4 (X: mullite, ●: quartz, ○: anorthite, Δ: gehlenite, C: cristobalite).

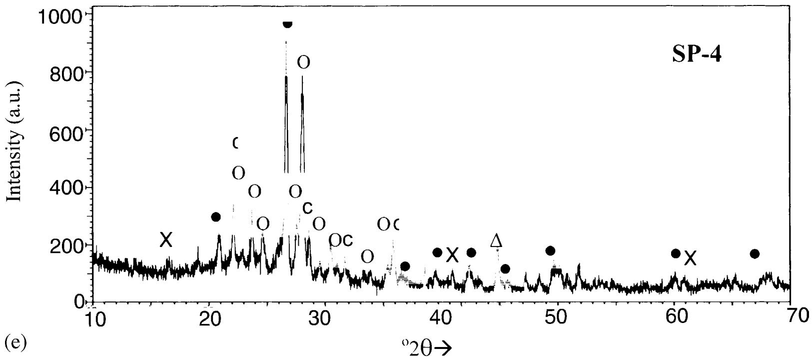


Fig. 3. (*Continued*).

and mullite were used as reference material. For reliability of data, each sample was scanned several times. The fitted curve matched well with the raw data and 'goodness of fit' varied from 2.5 to 4 among different samples. For scanning electron microscopy study, samples were polished to 1 μm finish with diamond paste after initial grinding with SiC powder and water. The polished surfaces of such samples were etched for 3 min in 5% HF solution at room temperature (35 °C), washing in water and acetone followed by gold sputter coating (Edwards, Scancoat six) for 5 min at 1 mbar pressure. SEM (LEO 430i) operating at 15 kV and 20 pA probe current was used for obtaining secondary electron images (SEI) of etched surfaces.

3. Results and discussions

3.1. Chemical analysis

Table 2 provides the chemical analysis of all the raw materials used in making experimental bodies. Kaolinite, feldspar and quartz are almost similar kinds that are commonly used in making traditional porcelain compositions.

Blast furnace slag contain CaO and SiO_2 as major constituents, enriched with Al_2O_3. Table 3 provides the oxide composition expressed as SiO_2:Al_2O_3 ratio, total alkaline oxides (mass%) and alkaline earth oxide (mass%). SiO_2:Al_2O_3 ratio and total alkaline oxides were found to be maximum in normal porcelain (NP) and minimum in SP-4 composition while total alkaline earth oxides content was minimum in NP and maximum in SP-4 composition.

3.2. Physico-mechanical characteristics

The variation in linear shrinkage (LS) and bulk density (BD); apparent porosity (AP) and flexural strength of 1200 °C heated samples with slag content are presented in Figs. 1 and 2, respectively. It may be seen that 5% slag addition to normal porcelain composition enhances the densification and strength significantly (increase in LS, BD and flexural strength, decrease in AP).

Further additions of slag did not alter the physico-mechanical properties much. In one of the earlier study of the present authors,[19] it was observed that normal porcelain of similar composition required around 1300 °C to achieve the same densification which is achieved in the present investigation by addition of 5% slag in place of feldspar. Even though 20% slag containing body (SP-4) has shown some small increase in porosity at 1200 °C, but its strength increases may be due to development of stronger pre-stress caused by the difference in thermal expansion coefficient between glassy matrix and crystalline phases.

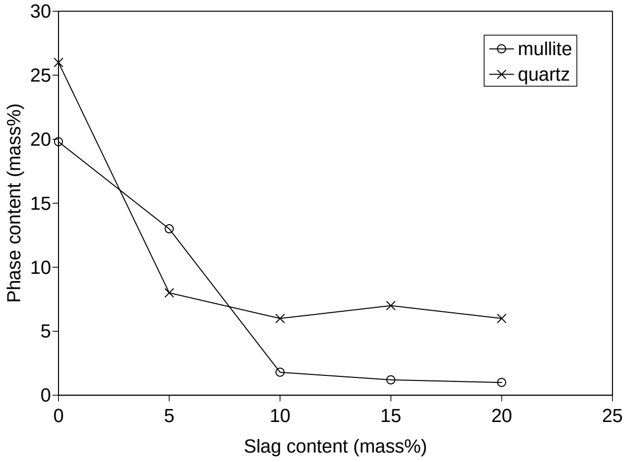


Fig. 4. Variation in phases with slag content.

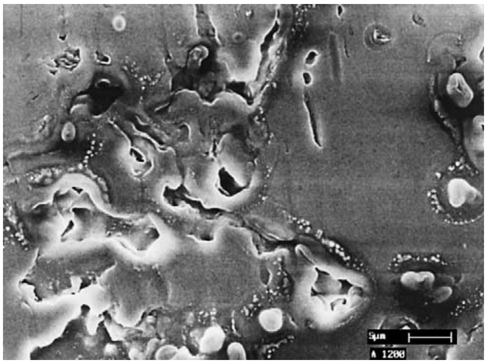
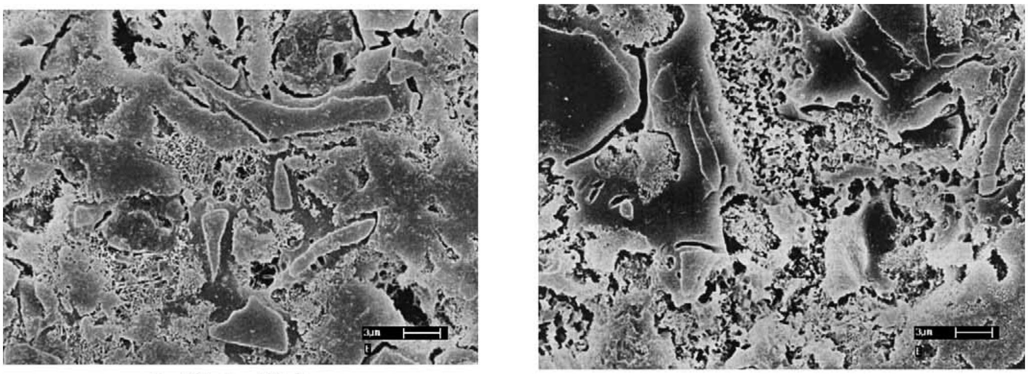
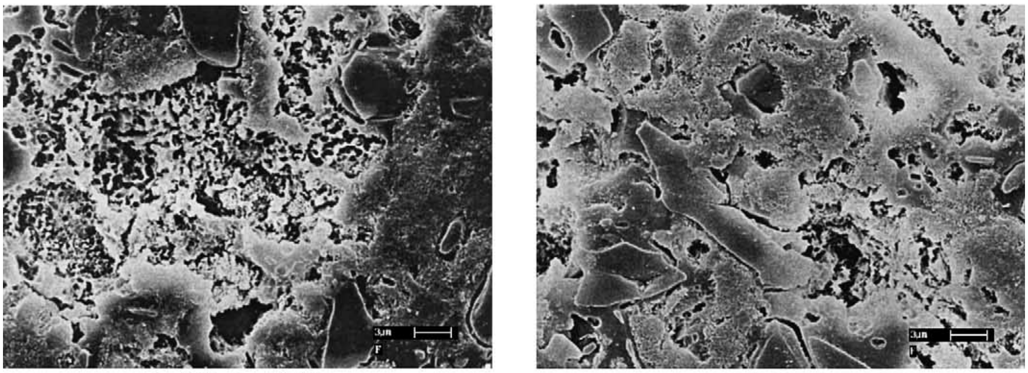


Fig. 5. SEM photomicrograph of 1200 °C heated normal porcelain.



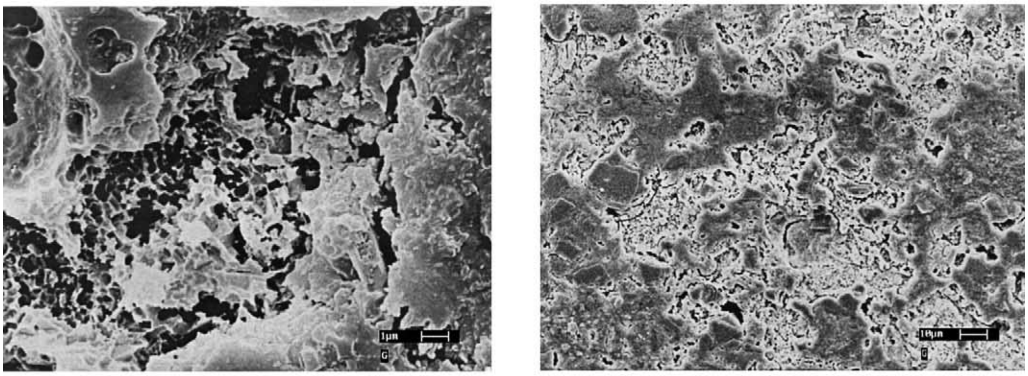
6a: 5% slag (SP-1)

6b: 5% slag (SP-1)



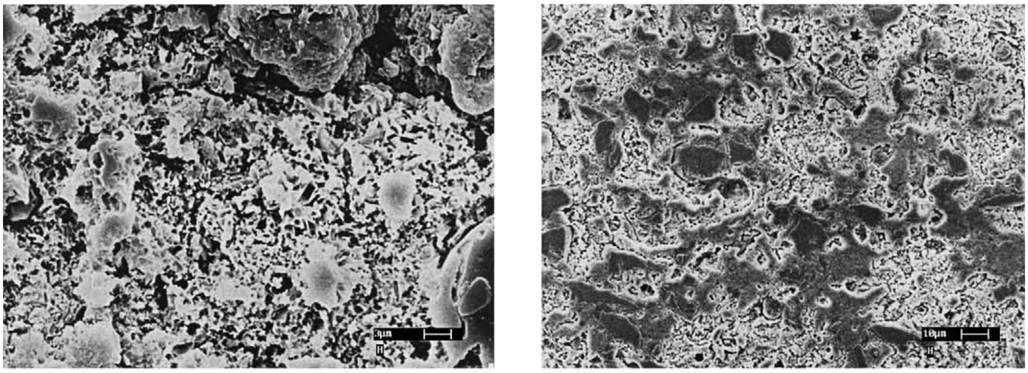
6c: 10% slag (SP-2)

6d: 10% slag (SP-2)



6e: 15% slag (SP-3)

6f: 15% slag (SP-3)



6g: 20% slag (SP-4)

6h: 20% slag (SP-4)

Fig. 6. (a–h) SEM photomicrographs of slag based porcelain heated at 1200 °C.

3.3. Phase analysis

The phase changes in the 1200 °C fired experimental bodies were investigated by X-ray diffraction analyses and the patterns are exhibited in Fig. 3a–e. The NP sample shows major XRD peaks correspond to α-quartz and mullite. Mullite peaks were seen up to 5% slag addition beyond which major mullite peaks were disappeared and anorthite peaks started appearing. Quartz peaks even though shows decreasing trend with slag content but it was always present in all the samples. Highest slag containing body (SP-4) shows anorthite and quartz as major phases. Several other small peaks in SP-2, SP-3 and SP-4 samples correspond to cristobalite, gehlenite and mullite. Formation of cristobalite and gehlenite phases in this type of slag-containing body was also noticed by other authors.[12,20] The weight percentages of quartz and mullite were quantitatively estimated by XRD and their variation with slag content is shown in Fig. 4. It may be seen from this figure that by addition of 5% slag in normal porcelain body, the quartz level is drastically reduced from 26 to 9 mass% and then remains almost unchanged on further addition. This reduction in quartz level is beneficial for a porcelain body as its presence in larger size causes major crack failure. Mullite level is also reduced from 20 to 14 mass% on 5% slag addition followed by drastic reduction up to 2 mass% on further slag addition.

3.4. Microstructure

The microstructures of all the 1200 °C heated samples are shown in Figs. 5 and 6a–h. Normal porcelain shows an uneven texture (Fig. 5), even though a liquid phase is present, it is not enough to cover the entire matrix. Certain amount of open porosity exists within the structure. Most of the feldspar crystal melted except a few of sizes 1–2 μm, which are partially melted indicated by rounding of their edges. Some mixed clay-feldspar relicts are also seen surrounding partially melted feldspar crystals.

No mullite and distinct quartz grains are observed in the NP sample at 1200 °C, even though their presence are detected by XRD. This is probably due to the presence of viscous glasses which are not properly etched away. As a result, quartz and mullite are not seen under secondary electron images. The samples of similar composition when heated at 1300 °C (more liquid formation) and etched under similar conditions, both primary mullite, needle shaped secondary mullite and quartz crystals were distinctly observed by the present authors in another study.[19] Fig. 6a and b shows the microstructure of 1200 °C heated 5% slag containing sample (SP-1). Overall microstructure (Fig. 6a) shows distinct presence of needle shaped mullite and quartz grains throughout the matrix. Appearance of anorthite phases are seen in Fig. 6b. Slag, containing considerable amount of CaO, SiO_2 and Al_2O_3 melted with feldspar, quartz and clay and the melted glassy phases crystallized as anorthite ($CaO{\cdot}Al_2O_3{\cdot}2SiO_2$).[21] The gradual disappearance of mullite and quartz crystals and presence of more anorthite phases are observed in SP-2 sample (Fig. 6c and d). Mullite crystals are almost disappeared in SP-3 sample containing 15% slag (Fig. 6e and f). Anorthite and quartz grains are clearly observed in these microstructures. Fig. 6g and h shows the microstructure of SP-4 samples containing highest quantity of slag (20 mass%) in the present investigation. The anorthite phases cover the entire surface (Fig. 6g) with few scattered quartz grains. Overall microstructure of SP-4 sample (Fig. 6h) shows the presence of anorthite grains and few quartz grains almost uniformly distributed in the glassy matrix. Circumferential cracks are observed around quartz grain probably due to larger difference in thermal expansion coefficient between glassy matrix, anorthite and quartz grains during cooling process. The stronger pre-stress thus developed may be responsible for increased flexural strength in SP-4 sample. Similar observation was also made by other authors that the strength of porcelain is influenced mainly by stresses developed in the glassy matrix rather than amount of mullite crystals present.[11] Tai et al. also produced anorthite based porcelain by addition of aluminous cement in place of clays in triaxial porcelain composition and reported the similar observation of stronger pre-stress development.[22]

4. Conclusions

Partial substitution of feldspar by blast furnace slag in a normal porcelain composition enhances the densification and strength. Mullite crystals present in normal porcelain body gradually reduced with increase in slag content and remains almost unchanged beyond 10% slag addition. Quartz level also reduced upto 5% slag addition beyond which remains unchanged. Distinct changes in microstructure also show gradual disappearance of needle shaped mullite crystals and reduction of quartz grains to a certain level. Microstructures of slag-containing bodies show the appearance of anorthite formed by crystallization of the melted glassy phase. The final microstructure of 20% slag containing body consists of anorthite, quartz, glass and minor amounts of cristobalite, mullite and gehlenite. The flexural strength of the 20% slag containing body is increased by the fewer crack origins due to stronger pre-stress.

Acknowledgements

The authors would like to thank Dr. H.S. Maiti, Director, Central Glass and Ceramic Research Institute, Kolkata, India for his kind permission to publish this research work, Prof. N.K. Mitra, Calcutta University, India for his valuable suggestions and encouragement during the course of this work. The authors express their thanks to Dr.(Mrs.)

Sudakhina Roy, CGCRI, Kolkata India for SEM studies. The authors also acknowledge the sponsorship of this research work by H&R Johnson (India) Ltd.

References

1. Iqbal, Y. and Lee, W. E., Fired porcelain microstructures revisited. *J. Am. Ceram. Soc.* 1999, **82**(12), 3584–3590.
2. Lee, W. E. and Rainforth, W. M., *Ceramic Microstructures*. Chapman & Hall, London, UK, 1994.
3. Klein, A. A., Constitution and microstructure of porcelain. *Natl. Bur. Stand. Tech. Pap.* 1916–1917, 3–38.
4. Lundin, S. T., Microstructure of porcelain. *Natl. Bur. Stand. (US) Misc. Publ.* 1964, **257**, 93–106.
5. Iqbal, Y. and Lee, W. E., Microstructural evolution in triaxial porcelain. *J. Am. Ceram. Soc.* 2000, **83**(12), 3121–3127.
6. Schuller, K. H., Reaction between mullite and glassy phases in porcelain. *Trans. Br. Ceram. Soc.* 1964, **63**(2), 103–117.
7. Ece, O. I. and Nakagawa, Z. E., Bending strength of porcelains. *Ceram. Int.* 2002, **28**, 131–140.
8. Braganca, S. R. and Bergmann, C. P., A view of whitewares mechanical strength and microstructure. *Ceram. Int.* 2003, **29**, 801–806.
9. Carty, W. M. and Senapati, U., Porcelain-raw materials, processing, phase evolution and mechanical behaviour. *J. Am. Ceram. Soc.* 1998, **81**(1), 3–20.
10. Ohya, Y. and Takahashi, Y., Acoustic emission from a porcelain body during cooling. *J. Am. Ceram. Soc.* 1999, **82**(2), 445–448.
11. Zsolnay, L. M., Mechanical strength of porcelain. *J. Am. Ceram. Soc.* 1957, **40**(9), 299–306.
12. Marghussian, V. K. and Yekta, B. E., Single fast fired wall tiles containing Iranian iron slags. *Br. Ceram. Trans.* 1994, **93**(4), 141–145.
13. Das, S. K., Kumar, S., Singh, K. K. and Rao, P. R., An innovative approach towards utilization of wastes generated from iron and steel industries. In *Proceedings of National Seminar EWM*, held in Jamshedpur, India, 1996, pp. 86–93.
14. Fiori, C. and Brusa, A., *Ceramic Powders*, ed. P. Vincenzini. Elseiver Scientific, Amsterdam, Oxford, New York, 1983, pp. 161–172.
15. Lenkei, M., Rozsnyoi, A. and Bansaghi, Z., *Ceramic Powders*, ed. P. Vincenzini. Elseiver Scientific, Amsterdam, Oxford, New York, 1983, pp. 173–182.
16. Dana, K. and Das, S. K., High strength ceramic tiles containing Indian metallurgical slag. *J. Mat. Sci. Lett.* 2003, **22**(5), 387–389.
17. Bandopadhyaya, A., Kumar, S., Das, S. K. and Singh, K. K., In the pursuit of waste free metallurgy. *N.M.L. Tech. J.* 1999, **41**(4), 143–162.
18. Dana, K. and Das, S. K., Some studies on ceramic body composition for wall and floor tiles. *Trans. Ind. Ceram. Soc.* 2002, **61**(2), 83–86.
19. Dana, K., Das, S. and Das, S. K., Effect of substitution of fly ash for quartz in triaxial Kaolin-quartz-feldspar system. *J. Eur. Ceram. Soc.* 2004, **24**(10–11), 3169–3175.
20. Ghosh, S., Das, M., Chakraborti, S. and Ghatak, S., Development of ceramic tiles from common clay and blast furnace slag. *Ceram. Int.* 2002, **28**, 393–400.
21. Levin, E. M., Robbins, C. R. and McMurdie, H. F., *Phase Diagrams for Ceramists*, ed. M. K. Reser. American Ceramic Society, Columus, OH, 1964.
22. Tai, W., Kimura, K. and Jinnai, K., A new approach to anorthite porcelain bodies using non plastic raw materials. *J. Eur. Ceram. Soc.* 2002, **22**, 463–470.