Effect of titania on fired characteristics of triaxial porcelain

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Abstract. Titania was progressively added in the range 3–9 wt% into a triaxial porcelain body consisting of clay, quartz and feldspar. The composed bodies were heated at five different temperatures in the range 1200–1400°C and their fired properties as well as phases evolved were studied. The results revealed that beyond 1300°C, formation of more liquid phases caused bloating in samples which led to generation of pores. This effect is more pronounced in TiO_2 containing samples. In the present system, 1300°C appeared to be the optimum temperature at which porosity was almost negligible and strength was maximum (45 MPa), particularly in presence of TiO_2. From the results of XRD studies, it was revealed that quartz content primarily decreased with increase in TiO_2 content due to excess glass formation and its subsequent dissolution. Mullite content increased with increase in TiO_2 content. No significant effect was observed beyond 6 wt% addition. Microstructure primarily showed the presence of quartz grain and cluster of smaller sized primary mullite crystals in both the samples without and with TiO_2. Very few secondary mullite crystals were also observed. SEM picture of sample containing 9 wt% TiO_2 showed some grain boundary crack due to cooling stress generated in the glassy phase. The drastic reduction of residual strength after 8 cycles of heating at 800°C and cooling particularly in TiO_2 containing samples suggests controlled heat treatment of the vitrified samples necessary to promote secondary crystallization process for the enhancement of strength. Attempts have also been made to correlate the constitutional parameters with the properties.

Keywords. Triaxial porcelain; titania; mineralizer; fired properties.

1. Introduction

The most significant development in the history of ceramics was the production of a vitrified, translucent porcelain body in china (Cox 1944). Although the term porcelain is sometimes applied to a variety of vitreous and near vitreous ware, it is more properly restricted to translucent vitreous ware. A wide range of triaxial ceramic compositions that are used in white ware industries basically contain clay, quartz and feldspar. The primary role of each of these raw materials in triaxial bodies are discussed earlier (Lundin 1959; Norton 1970; Carty and Senapati 1998). In these compositions, clay serves a dual purpose of providing fine particle size and good plasticity for forming. Feldspar acts as a flux, forming a viscous liquid at firing temperature and aids in vitrification. The quartz is mainly an inexpensive filler material which remains unreactive at low temperature of firing and forms a highly viscous liquid at higher temperatures. The main differences between the compositions are in relative amounts and kinds of feldspar and clay used. Mullite ($3Al_2O_3 \cdot 2SiO_2$), a-quartz and glass contribute major portion of porcelain

microstructure in triaxial based clay–quartz–feldspar system (Lundin 1964). Lundin (1959, 1964) also indicated the formation of cristobalite phases when the rate of transition of quartz to cristobalite exceeds the rate of quartz dissolution. Schneider *et al* (1986) showed that the transformation of quartz to cristobalite can be accelerated by high crystal defect density and small particles. The potential for cristobalite formation however, becomes less likely. Several researchers (Comer 1960; Schuller 1964; Lundin 1964; Klug *et al* 1987, 1990) discussed the mechanism of mullite formation in porcelain bodies. Concentration gradient and diffusion rates of alkalis are the two important factors that affect mullite formation as reported by Lundin (1964). While Comer (1960) described the formation of mullite on the surface of clay relicts, Lundin (1964) proposed that this mullite in clay relicts serves as a seed for nucleation and crystallization in the feldspar relicts. As alkali diffuses out of feldspar at higher temperatures, secondary mullite in the form of needle shape nucleates and grows. Heating schedule has a crucial role to crystal morphology and structure of mullite within the glassy matrix of porcelain. Pask and Tomsia (1991) reported the formation of spinel structure at lower temperatures of slow heating which converts to orthorhombic mullite by reacting with silica. Fast heating rates lead to

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tetragonal mullite formation at temperatures as low as 980°C followed by orthorhombic mullite formation at higher temperatures.

Mineralogical compositions of porcelain bodies have been widely studied (Parmelle and Rodrignez 1942; Zografon 1968; Mackenzie 1969; Chaudhuri 1974; Johnson and Pask 1982; Maslennikova and Stoikova 2001) with special reference to the influence of some mineralizing agents on the development of the crystalline and glassy phases at higher temperatures. The mineralizers enter the glassy phase of the porcelain samples and modify the solubility of mullite in glass. Johnson and Pask (1982) reported that impurities such as Fe_2O_3 and TiO_2 affect the kinetics and morphology of mullite formation and that the exsolution of silica facilitates mullite formation in kaolin. Chaudhuri (1974) observed maximum and minimum mullitization in the porcelain samples containing 2% Fe_2O_3 and 4% ZnO, respectively. ZnO up to 1% and 2% TiO_2 promote development of mullite; whereas Fe_2O_3 continues to produce a higher yield of mullite in hard porcelain up to 4%. More than 1% ZnO makes the glass corrosive to mullite whereas up to 2% TiO_2 prevents attack of mullite by glass. Zografon (1968) reported that 1 to 3% TiO_2 could be tolerated in the glass without inhibiting mullitization. Porcelain is a semivitrified body consisting of both crystalline and glassy phases and the latter plays an important role controlling the major properties. In the present investigation the TiO_2 content was varied between 3 and 9% with the intention to study its effect on primary mullite formation from dehydroxylated kaolinite and also to change the composition of the glassy phase leading to crystallization which may improve grain boundary condition. Fe_2O_3 was found to be the most efficient mineralizer at higher concentration level. The residual quartz and glass can react in presence of certain mineralizers by a two-step process i.e. replacement of Al^{3+} ion from glass by cation of the mineralizer and subsequent diffusion of Al^{3+} ion into the residual silica. The mineralizing action of a cation is dependent on the ease with which it can penetrate into the proper structure. Radii and potential of the cation and the cation oxygen bond strength have been suggested to be the factors controlling penetrating power of the cation. Mackenzie (1969) studied the effect of 28 exchangeable cation on the formation of mullite from halloysite. He observed different kinds of reaction mechanism between alkaline and alkaline earth cation and transition metal cation.

In the present investigation, TiO_2 was incorporated progressively into a parent triaxial porcelain composition and its effect on the physico-mechanical properties was studied. Qualitative estimation of quartz and mullite was done to indicate the influence of TiO_2 on such composition using X-ray diffraction studies. Microstructural features of some selected samples were also examined through SEM of the polished and etched surface of the vitrified specimens.

2. Experimental

The major raw materials used in the study were collected from Indian source (China clay from Rajmahal, Bihar; Ball clay from Bikaner, Rajasthan; quartz and feldspar from Ranchi, Jharkand). For chemical analysis of these raw materials, gravimetric method was utilized to determine SiO_2 and Al_2O_3 whereas Fe_2O_3, CaO and MgO were estimated volumetrically (Hillebrand and Lundell 1953). Alkalies were determined by flame photometry. Titania (TiO_2) was of pure chemical grade (BDH quality, E-Merck India Ltd.). One kilogram of each batch (A, B, C and D) were prepared according to the batch compositions presented in table 1. All the batches were mixed separately and wet ground in a pot mill for 8 h to get the desired fineness (residue < 1·5 wt% on 200 mesh BS sieve). The slurry obtained was screened, dried at 110°C and powdered to break the agglomerate. A part of the powdered batches was calcined separately at 900°C with a soaking period of 2 h to remove all types of water from the mixture so that during firing undue shrinkage may be avoided. 85 wt% of the calcined batch was again thoroughly mixed with 15 wt% of uncalcined batch and 2% PVA solution as binder. Required amount of water was sprayed on the mixture and granulated to small particles for better compaction.

Samples ($60 \times 14 \times 5$ mm) were hydraulically compacted using uniaxial pressing at 350 kg·cm^{-2}. The bar samples were dried at 110–120°C till the moisture content reduced to < 0·5%. The dried samples were fired at five different temperatures (1200, 1250, 1300, 1350, 1400°C) for a soaking period of 120 min in an electrically operated laboratory furnace using a on/off control system. A constant heating rate of 10°C/min up to 1000°C and 5°C/min up to the peak temperature was maintained in each firing. Finally, the fired samples were subjected to physical tests such as linear shrinkage, ap-

Table 1. Batch compositions (wt%).

Batch	China clay	Ball clay	Feldspar	Quartz	Titania
A	40	10	25	25	Nil
B	38·8	9·7	24·25	24·25	3
C	37·6	9·4	23·50	23·50	6
D	36·4	9·1	22·75	22·75	9

parent porosity and bulk density. Bulk density (BD) and per cent apparent porosity (AP) of the fired samples were measured using conventional liquid displacement method according to Archimedes principle. Flexural strength (three-point bending) of the fired samples was determined by universal testing machine (INSTRON 5500 R). The results of all these testings reported here are the average of six samples. Philips 'X-pert Pro' diffraction unit, with secondary monochromator, automatic divergence slit and nickel filter (Cu-Ka radiation) was used to identify the various phases formed in vitrified samples. XRD studies were carried out with powder (– 200 mesh BS sieve). For SEM study, samples were polished to 1 μm finish with diamond paste after initial grinding with SiC powder and water. The polished surface of each samples were etched for 3 min in 5% HF solution at room temperature (350°C), washed in water and acetone followed by gold sputter coating (Edwards, Scancoat). SEM (LEO 430 i) was used for obtaining secondary electron images.

3. Results and discussion

The results of chemical analysis of the raw materials are given in table 2. The chemical analysis results indicate that china clay, ball clay, quartz and feldspar are of normal type generally used in porcelain body with minimum amount of impurities.

The results of linear shrinkage are graphically represented in figure 1. It may be noted from this figure that the temperature effect was not linear. Linear shrinkage increased with increase in firing temperature up to 1300°C followed by significant decreasing trend up to 1400°C. This might be related to the formation of more liquid phase causing bloating (generation of pores leading to expansion). This trend was observed with all the compositions. It may also be observed that shrinkage increased with increase in TiO_2 content. This may be explained in the way that TiO_2 increased the rate of reaction. In presence of TiO_2, shrinkage increased sig-

Table 2. Chemical analysis of raw materials.

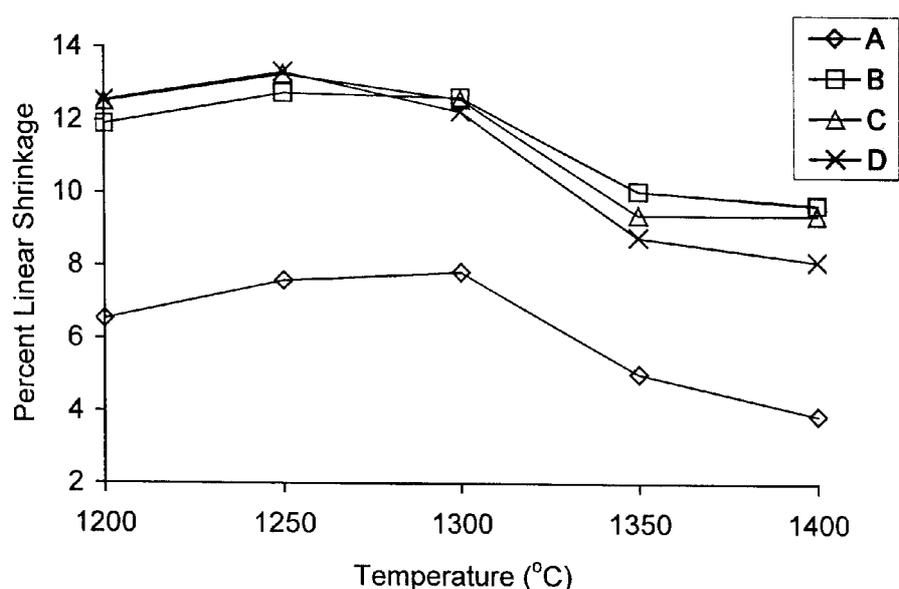| Major chemical constituents (wt%)	China clay	Ball clay	Quartz	Feldspar	Titania
SiO_2	45·41	59·25	98·66	66·48	–
Al_2O_3	34·39	30·75	0·39	17·29	–
Fe_2O_3	1·13	1·23	0·07	0·14	< 0·07
TiO_2	0·89	0·52	0·01	0·02	98·00
CaO	1·07	0·34	0·10	0·31	–
MgO	0·76	0·25	0·02	0·03	–
K_2O	0·42	0·82	0·12	11·95	–
Na_2O	0·87	0·27	0·09	2·94	–
L.O.I.	14·67	10·50	0·37	0·71	0·50

Figure 1. Variation of linear shrinkage with temperature of heating.

nificantly which might be due to enhanced crystallization (mullitization) and formation of more flowable glassy phase. TiO_2 containing samples exhibited similar nature of curves. Initial rate was slow compared to that without TiO_2. Two inflection points were observed, first one at 1300°C which was very sharp with TiO_2 containing samples. The second one at 1350°C where the slope was small. The shrinkage in this type of triaxial system was due to removal of residual amount of water from clay, decomposition of binder, liquid formation from the flux as well as generation of crystalline phases from amorphous materials. The results indicated that the pyrochemical reactions in this type of compositions did not attain equilibrium under the present experimental conditions. From the physical appearance of the fired samples, no distortion or sagging was observed. The formation of glass and simultaneous dissolution and subsequent reprecipitation of crystalline phases are the main controlling factors leading to shrinkage and expansion. The extent of primary reactions amongst the different ingredients was indicated by the first inflection point i.e. shrinkage maxima. The general trend of interaction remained more or less same at all compositions, only the magnitude differed. This type of interaction is a case of viscous composite sintering which involves much larger liquid contents than liquid phase sintering.

The results of apparent porosity are presented in figure 2. It is revealed from the figure that porosity decreased
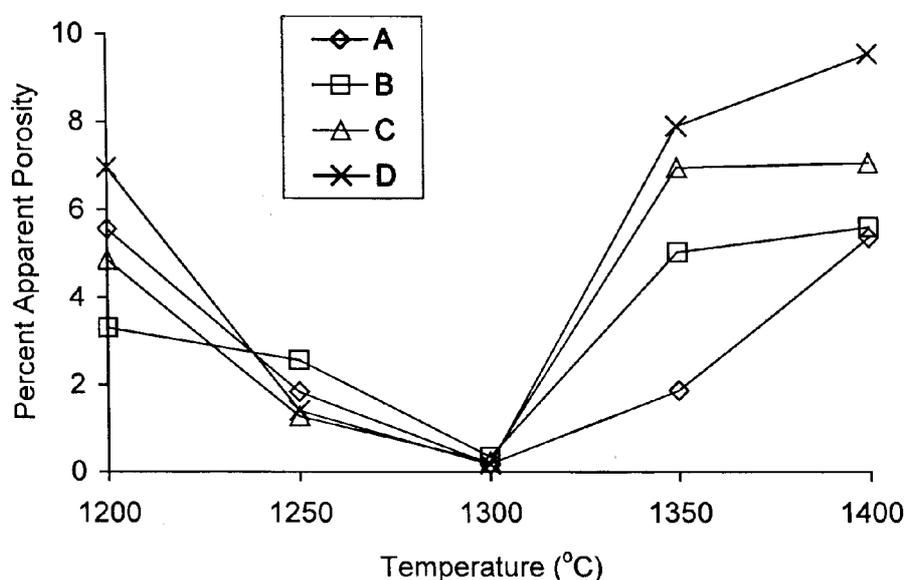

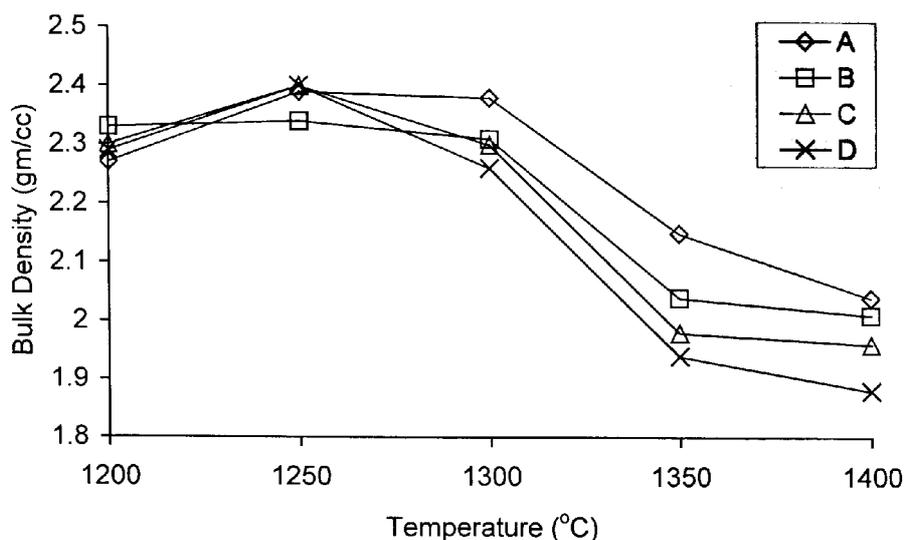**Figure 2.** Variation of apparent porosity with temperature of heating.

Figure 3. Variation of bulk density with temperature of heating.

with increase in firing temperature due to material transport into the pores as well as migration of glassy phase therein also. This trend was followed up to 1300°C beyond which it increased again. The latter phenomenon was due to bloating action leading to pore formation in a vitrified mass. Minimum porosity was noticed at 1300°C. Thus, it may be said that in this particular system, 1300°C appeared to be the optimum temperature at which apparent porosity was almost negligible particularly in presence of TiO$_2$. The relationship between bulk density and firing temperature has been shown in figure 3. The results show that the composition without TiO$_2$ exhibited increase of bulk density up to 1300°C following which it decreased. Titania promoted the reaction that was evident from an increase of bulk density at earlier temperature (1250°C). At higher temperature, the rate of change of bulk density was significantly high. Moreover, the curves were analogous to the corresponding shrinkage curves.

Variation of room temperature flexural strength with temperature is shown in figure 4. From the figure it is revealed that this triaxial body either in presence or absence of TiO$_2$ showed maximum strength at 1300°C following which it decreased. The latter phenomenon may be related to the formation of more glassy phase which probably effect the proper interlocking of mullite needles in the microstructure. At 1300°C, flexural strength increased with increase in TiO$_2$ and maximum strength achieved was 45 MPa. The nature of the curves was identical indicating that same mechanism was followed at all TiO$_2$ contents. The increase of bending strength with 9% TiO$_2$ was not significantly high compared to 6%, only a marginal increase which might not be totally related to mullite formation but alignment of mullite crystals, their growth characteristics and nature of the glassy phase. With increasing TiO$_2$ content there was a strengthening of the decomposition of mullite thereby increasing the amount of glass and aluminium titanate.

Substitution of Al^{+3} by Ti^{+4} probably in the octahedral sites of mullite crystals could cause aluminium ion vacancy according to following reflect reaction

$$(1 - X) \, Al_2O_3 + X \, TiO_2 \longrightarrow 2(1 - X)$$
$$Al_{Al} + X Ti_{Al} + X/3 \, VAl^{III} + (3 - X) \, O_O,$$
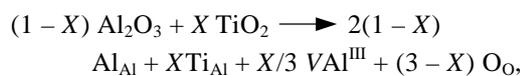
which enhances mass transport and consequently reaction rate. Lattice parameters and unit cell volume for solid solution series increased with increasing amount of foreign oxide. The TiO$_2$ contributed defect formation during reaction. From 1300°C, the rate of decrease of strength on increase of temperature was faster than the corresponding increase from the earlier temperature. Initially, TiO$_2$ entered into mullite grain by solid solution formation without much change in composition or amount of viscous phase. At higher temperature, the lower strength value was due to change in composition of the glassy phase. Elastic bond relaxation at high temperature might be also a contributing factor.

The samples heated at 1300°C was subjected to thermal shock (repeated heating at 800°C and cooling) and the results of residual flexural strength after eighth cycles of alternate heating and cooling are given in table 3. Drastic reduction of strength occurred and this was accelerated by the presence of TiO$_2$. This might be related to the formation of low viscosity glass. This finding suggests that this type of body containing TiO$_2$ as additive should be further heat treated to effect crystallization

Table 3. Residual flexural strength.

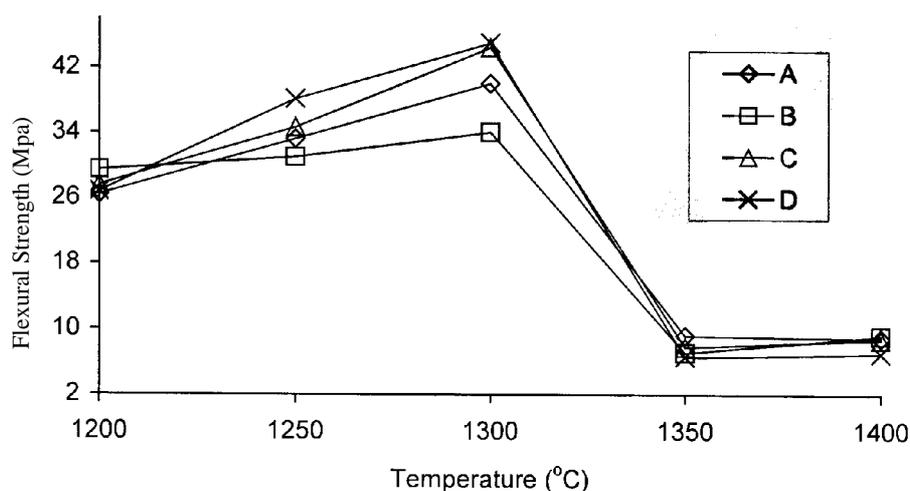| Batch	Flexural strength (MPa)
A	5·98
B	2·77
C	2·40
D	2·79

Figure 4. Variation of flexural strength with temperature of heating.

from the glass phase for the enhancement of mechanical properties as well as thermal shock resistance.

The most important aspects related to thermal interaction among the ingredients and generation of newer crystalline phases were done by carrying out X-ray diffraction analysis. The diffraction pattern of 1300°C heated samples have been represented in figure 5. In all the patterns, quartz and mullite were found to be the major crystalline phases. From the peak heights, it was evident that quartz content primarily decreased with increase in TiO_2 content which might be due to excess glass formation that caused some dissolution of quartz. It may also be observed that mullite content increased with increase in TiO_2 content and no significant effect was observed beyond 6 wt%

addition. The SEM photomicrographs taken on some selected polished and HF etched samples show the presence of quartz grain and cluster of smaller sized primary mullite crystals in both the samples (figures 6a and b). Very few secondary mullite crystals are observed. The morphology of mullite grains is very much dependent on TiO_2. At higher concentration it accelerated grain growth which was observed with batch D (9% TiO_2 containing sample). This growth led to some grain boundary crack due to cooling stress generated in the glassy phase. This observation suggests that if TiO_2 containing samples were subjected to further controlled heat treatment at lower temperature the secondary mullite could have developed by secondary crystallization process.
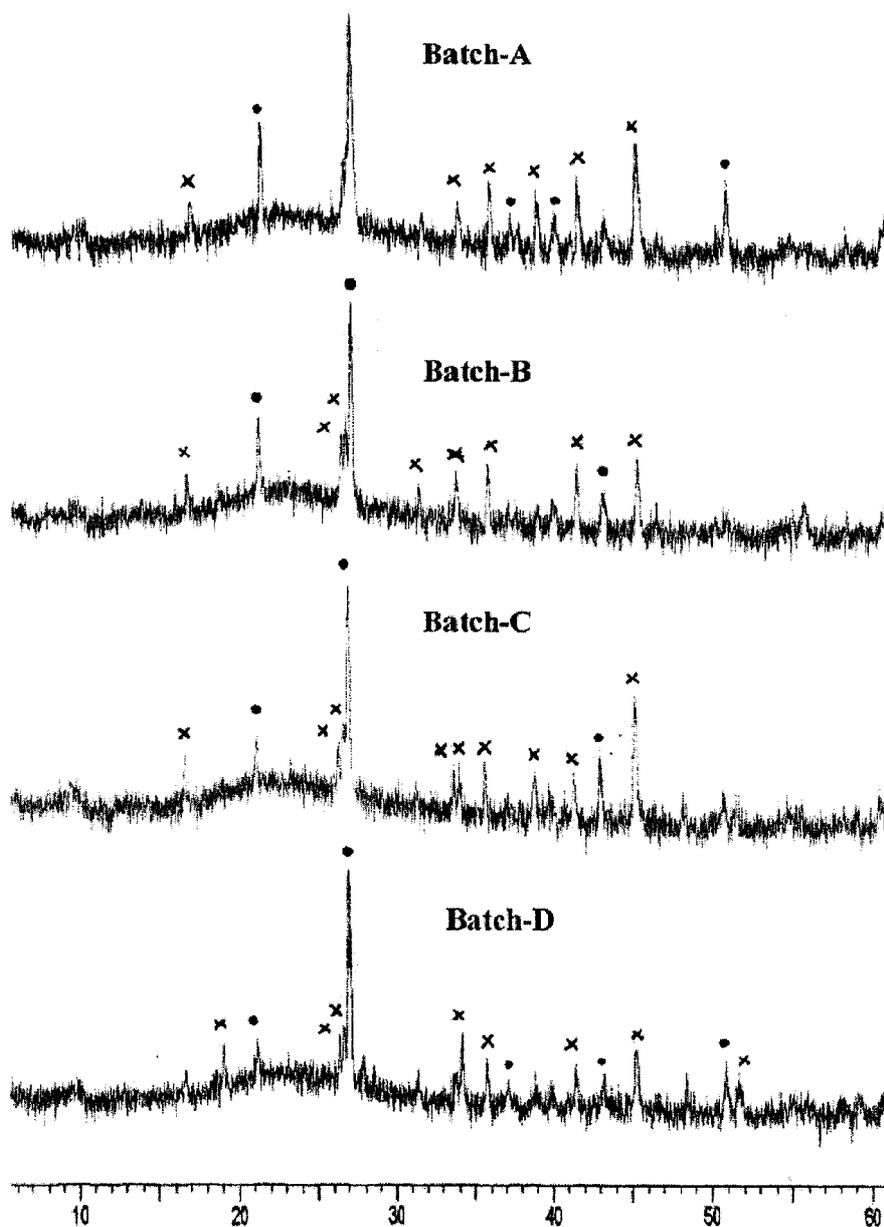

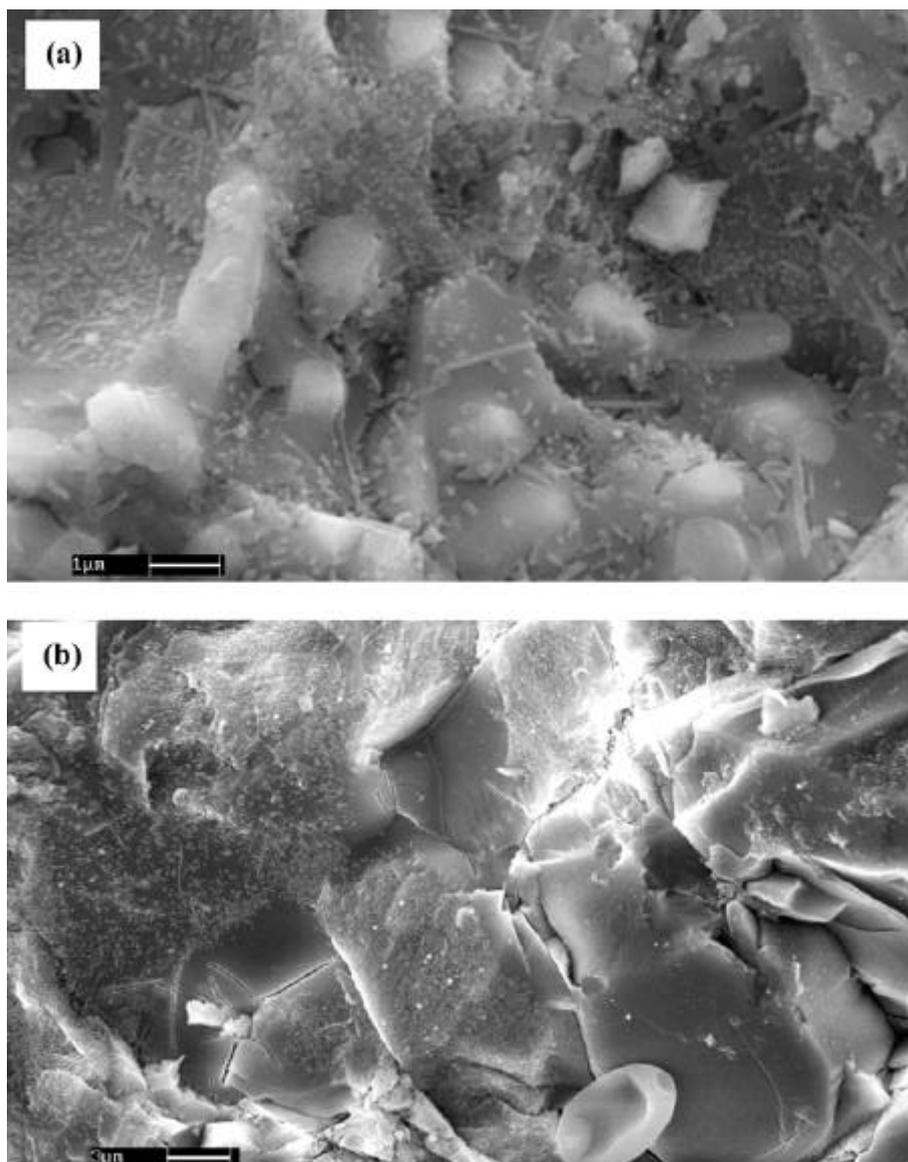**Figure 5.** XRD pattern of different batches fired at 1300°C (●, quartz; ×, mullite).

Figure 6. SEM photomicrographs of samples heated at 1300°C (polished and etched): (**a**) batch A and (**b**) batch D.

4. Conclusions

The standard triaxial porcelain body either in presence or absence of titania showed optimum physical properties and maximum strength at 1300°C following which the properties deteriorated. The effect is more pronounced in TiO_2 containing samples due to excess formation of glassy phases. XRD results confirmed the presence of quartz and mullite as major phases. Quartz content decreased with increase of TiO_2 content due to excess glass formation and its simultaneous dissolution while mullite content increased with TiO_2 content. SEM photomicrograph show the presence of quartz grain and cluster of smaller sized primary mullite crystals with very few secondary mullite needles in both the cases. The drastic reduction of residual strength particularly in TiO_2 containing samples after repeated heating and cooling suggests controlled heat treatment necessary in order to promote secondary recrystallization for the enhancement of strength and thermal shock resistance.

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