INTRODUCTION

X-Ray diffraction, pétrographie microscopy and SEM analysis are used together to obtain qualitative aod quantitative information on the microstucture of kaoilinite-illite-quartz bodies,.. The pétrographie- microscope is used to analyse of the microstructure and mineralogy of the fired products. Bur the results have not been entirely satisfactory because of the inability to detect crystalline particles, of submicrometer mulHte, cristobalite and pores, The. body consists of mullite cristobalite and quartz (crystalline phases) in a composite structure where crystals and porosity are embedded in the matrix of amorphous/glassy phase.. Both glass and amorphous phases .appear in more or less significant amounts in all the studied fired clay bodies., The presence of quartz, detrital mica, and Ca-Na feldspar indicate bodies-being usually fired under nonequlibrium conditions and that many chemical reactions do not go to completion because of the lack of sufficient, heat treatment and of intimate contact of the constituents. If the reactions were allowed to go to completion this would result in a large glassy phase that would endanger the desirable properties of the clay based ceramic bodies.

MATERIALS AND METHOD

The changes in the crystalline aod glassy phases were studied with the aid of .SEM micrographs obtained from, the fired bodies of kaolinite rich HB, mixed HK (%50HB+%50KW), illite rich KW and their feldspar mixed bodies on which tests of XRD, as well as thin section studies aod physical properties had been made. SEM observations were undertaken 011 etched fresh broken surfaces of the above mentioned bodies after coating with gold, They were examined at 20-30 k'V accelerating voltage with a Jeol XSM[1] 6400 equipped with, a Link energy dispersive spectrometer for qualitative analysis of chemical coin position of the selected points or areas,. The peak heights for the same element of different spectrums were used as a measure for the individual element concentration.,

The fractured fresh surfaces were treated during 1,2 minute or 3 minute with hot and cold HF. Figure 1-a, b, c, d, e aod f were taken from a fractured surface of wet mixed HK body fired at 1200°C, The specimen was etched with hot HF for 1 mie and coated with gold. Treatment with hot HF produces much more solution cavities and pits in amorphous/glassy phase. These small rounded aod tiny elongated etch pits tended to develop in size and depth with, increasing leaching time:., The micrographs of Figure 2 was taken from kaolinite rich (d, e, f) and, feldspar mixed bodies (a, b, c). HF treatment also resulted in, the formation of new crystalline phases that were precipitated from leaching solutions (Figure 3-a* b, c, d, e, f), The immediate washing with water after etching eliminated the new formed crystals on. etched .surfaces., They are all fired also at 1200°C.

RESULTS OF SEM OBSERVATIONS

As shown, in Figüre 1 a„ b aod c the quartz grains have been rounded by partial dissolution,. The crack patterns are severe and numerous around the larger quartz grains as well as. within, the glassy matrix. In the microphotograph a» it is difficult to differentiate: the porosity and the solution, pits of the- glassy phase. This dissolution pattern, shows that the amorphous/glassy phase has not a, homogeneous composition and structure,. The difference between the etched amorphous/glassy surface, the original quartz and the fresh cracked, surface are clearly seen on the micrographs of Figure 1 b. As shown, in the same micrograph, the new formed crystal on the fresh cracked surface of quartz, confirmed the curved structure on the original, quartz surface (Figure c) which is not produced by HF treatment., This curved structure may indicate cristobalite formation. Tuttle and Cook. (1949) have confirmed its presence by X Ray identification.,

SEM micrographs, also show actual pore sizes developed in the fired bodies. In Figures 1- d, e it is seen that at 1250°C, the bodies have three kinds of pore size dimensions. But according to the spatial distrubution of porosity observed in SEM, the poro-

sity in the fired body can be divided into intragranular and intergranular.

-The intragranular pores refer to pores within the original grains; they are small and produced by bubbling; and blistering;., They can be subdivided into 5-10pm and. ljim-<ljim. (Figure 1-d)

-The intergranular porosity consists of elongated shrinkage pores; they are large and. formed among; the grains (quartz and clay grains) and its size, changes between 20-50pm (Figure 1-e),

In the Figures .1 e, f coarser grains of K feldspar have glass in which the best development of mulllite occurred but nearby grains that contain, more bubbles and blebs have not mullite. The long; needles of mullite were more developed in the less viscous K-feldspar glass than in the more viscous K-feldspar glass. Therefore the absence of mullite in some of the K-feldspar-glass was assumed, to be indicative of relatively higher viscosity t:han that the of nearby grains,» filled with mullite,. The presence of blebs in this mullite-free feldspar glass, supported this, assumption the gas was retained by grains of higher viscosity but escaped easily from those of lower viscosity. Local impurities, in feldspar may have caused differences in viscosity of the individual, grains. On the other hand, many authors pointed out that the amount of mullite, formed in the feldspar glass, should, depend not only on the viscosity but also *on* the time afforded for molecular diffussion from the. clay glass.. Bubbling and blistering; in the glassy phase, depends not only on the viscosity but also on the- heating rate.. Bubbles in the feldspar glass are caused by the evolution of dissolved gases,. The gradual escape of some of these gases during a slow temperature rise accounted for the scarcity of bubbles,, In rapidly heated, specimen, insufficient time for the gradual escape of gas. resulted in the production of numerous bubbles,.

Primary mullite arises, mainly from the clay areas, while growth of secondary mullite occurs essentially within the feldspatic glassy zone: or relict feldspar grains (Figures. 2 a, b, c). During firing;, the K-feldspar grains start, to melt .above 1000°C There is. no change in the shape, because of the high viscosity. Smaller grains disappear by reaction-with the surrounding clay and the larger ones, interacts with the clay (alkali diffuse out of the feldspar and mullite crystals are formed in a glass)., Therefore, the outlines of glass-muUite areas correspond with, the original feldspar grains (Figures 2- b, c). The lath-shaped mullite crystals have well-defined outlines and their dimensions are rather constant (thickness less than 1pm. arid length larger than 2|im) in the relicts of feldspar (Figure 2 c). The primary mullite developed in clay has dimensions in the magnitude of nanometer and. the outlines of crystals are- not. well defined because of a. diffuse image at higher magnification (Figure 2.1)., The crystals have continuous development, in. the clay/amorphous matrix. Therefore mullite is. the crystalline phase in both the original feldspar/glassy grains and. in the clay amorphous/glassy matrix.(Figure 2- d, e, f) The crystal size and development are: quite different larger mullite needles growing, into the feldspar relicts from, the surface as the composition changes by alkali., diffusion. The formation, of mullite within the clay would not be observed on the thin, sections even, not at 1250°C firing., But SEM studies provide: important contributions to the understanding of the- differences in primary and. secondary mullite formations-

Energy dispersive X Ray analysis (EPX)

The presence of phases determined by X-Ray diffraction analysis is confirmed by means of energy dispersive X-Ray analysis (EDX).. The phases, are:

-primary and secondary mullite,

-clay and feldspar amorphous/glassy phase,

-Fe and Ti rich impurities

and. there is a new formation of calcium or potassium aluminosilicate crystals which are formed with different morphology on etched surfaces.. EDX data were also obtained, from this new formation.

In general EDX data were obtained, in

-scan mode with the beam, rastered over areas, as

large as 30H0A x 401)I)A' (corresponding higher magnification (X 3UUUÜÜ) and

-stationary point beam analysis mode..

The scan mode anahsis for pimiaiy and secondai y mıılhlc analysis include also glass\ mateiials, because tht above-mentioned minimum aiea is larger than the nbseived mullile ervslal si/c. The stationär) point mode anahsis diagiain (Figure 4 a, b) is obtained on the seeondaiy mnlhtc ciystal and the matiix, displays only a strong peak of AI and a ıclatneh small peak of Si.'On the amorphous glass} maliix the reverse is obser\t\î a with sinnig peak of Si and relatively small peak oi VI 11 lgure 4 e I. But the scan mode anahsis diagiam of the same secondai} mullite displays Al, Sı and weak K, *Cd,* Ti ami *Vc* peaks he cause the analyzed aie\i IN I-MI honing jnou s The obtained image *o*\ pjjiiuu\ nuillite at higher the magnification measured in nanometei is not used !nr point analysis because the deteetor position ot ihe low woiking distance (7,6 mm I hindeied LDX anahsis. For this icasun EDX diagrams oi selected areas with primary nuillite include amorphous/glassy phase ie suiting in lower Ai/Si ratio and higher K. Ca. Tu Fe peaks.

The HF etching developed new crystals on the leached, surfaces of the SEM samples,. The EDX spectrum of this new crystals displayed strong K and. Ca and relatively weak of Si and Al indicating that these aluminosilicates were rich in K and. Ca (Figure 4 e,, f).. It is widely accepted that dissolution of glasses is ineongruent. The chemical composition of new crystals indicate selective leaching of alkali ions from the amorphous/glassy matrix; therefore leaching also produces a dealkalized layer., In Figure 3 A, B the etching developed as gel-like grains exhibiting spherical humps on the surface of Ca-Na feldspar mixed bodies.. The EDX diagram of this material displays a strong peak of Ca and relatively small/peaks of Si and Al (Figure4- e). The SEM microphotograph of figure 3 d, e, f show the different K and Na-rich crystals appearing as hexagonal platy, lath and cubic-shaped and. twinned crystals. The EDX .spectrum of the hexagonal platy crystals shows strong K and Si and. small peaks of Al, Ti and Na (Figure 4 d). The EDX diagram of the twinned crystals show strong Si and relatively low Na and Al (Figure 4 F). The EDX diagrams of lath and small cubic shaped crystals are given in the same chemical composition. The variation in chemical composition, of these new crystals precipitated from leaching solutions of glasses indicate different chemical composition and incongriie.nl leaching of amorphous/glassy phase..

DISCUSSION AND CONCLUSIONS

-The characteristic needle-like habit, of mullile crystals is not observed in the amorphous/glassy matrix under the optical microscope since the primary niullite crystals, developed directly from amorphous clay are not large enough; however they are identified by the SEM studies..

-K-feldspar relicts consist of glass and mullile (<lu thickness,, lO-Sp length). The outlines of glass-mullite areas correspond to the original, feldspar grains and the unresolved, matrix, correspond to the amorphous/glassy grains of clay,.

-SEM observations show the diffference of the primary and secondary mullite formations,. The larger mullite needles grow in the K feldspar relicts (thicknees less than ljuini and length larger than 2[un) (crystallized in the oie.lt) but the eliptic shaped primary mullite in the clay amorphous/glassy phase has dimensions in the magnitude of nanometers (formed by a reaction, in the solid state)

-A. study of the amorphous and. .glassy phase remains one of the most important problems in the consideration of the fired bodies., Finally two types of amorphous material may exist together., i.e. a phase where the- crystal structure has been destroyed, (so that no characteristic X Ray peaks can be observed),. The composition and. structure of the amorphous and glassy phase are constantly undergoing changes during the heat treatment and the glassy component increases, On the other hand the transformation in. the crystalline state takes place very gradually and under high viscosity conditions so that the true .glassy state

is not immediately established because- equilibrium conditions are not attained during, the firing, time at 1150-.1250°C. Amorphous material and glass are not determined 'qualitatively because of the ambiguity in distinguishing different phases in samples fired 1150-1250°C. Inclusions, blebs and bubbles in the glassy grains, and their shapes helped, in the process of identification of the glasses,.

Microscopical examination of thin sections and SEM observations show only

-shrinkage pores at the peripheries of segregated clay aggregates (Intergranular)

-flaw patterns in the peripheries and inside of the quartz, (Intergranular)

-sealed pores in the amorphous/glassy matrix (Intragranular)

During firing at 1150°C, elongated shrinkage pores, firstly become, maximal, then are. partly healed, and the amount of sealed porosity increases,. The quartz flaws occur at cooling. The initial small micropores disappeared, and the larger shrinkage pores grew. All these observations showed that as the porosity decreases, the distrubution of the pore size shifted to a larger size with increasing temperature.

REFERENCE

Turtle, MA., Cook,,, **R.L.,1949 Fundemental** study of crystalline and glassy phases in whiteware bodies **J.Amer.Ceram. Soc.** 32. 9 279-294