Original Article

Deep inside the ceramic texture: A microscopic–chemical approach to the phase transition via partial-sintering processes in ancient ceramic matrices

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High-resolution microscopy investigations on ancient ceramics recommend the complex progression of crystalline phases in an antique object via the sintering process. Based on materials-science point of view, sintering is not a routinely reaction in all crystalline phases with the same crystallographic pattern, but also is a transition pathway. Sintering depends on the processing of raw materials via the manufacturing process. Five samples are chosen for this analytical approach from two different periods from Tappeh Zaghe, Iran (5100 millennium BC). A multimicroscopical approach was carried out by means of polarized light microscopy, environmental scanning electron microscopy, and atomic force microscopy. Crystalline phases were determined by X-ray diffraction and refined after Rietveld method. The observation of the behavior of phase–interphase boundaries of a crystalline part in the nano area suggests that the partial sintering is the point at which the mineral began to be decomposed, and the conditions of the occurrences of this phenomenon depend on crystallographic properties.

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1. Introduction

The ceramic-manufacturing process is one that is achieved by a high-temperature operation. Indeed, after a well-given temperature called the sinter temperature, the originally clayey body and additives decompose to a sintered body. Many ancient ceramic materials are often defined as earthenware materials based on their raw-material usage (red earthenware clay, calcareous, or siliceous) and manufacturing temperature (950–1050 °C) [1]. For dispersion-strengthened ceramics, the particles have normally smaller diameters, ca. 0.01–0.1 μm (10–100 nm). The particle–matrix interaction, which is also responsible for strengthening, occurs at the atomic or molecular level of their constituents. The mechanism of strengthening is similar to that for hardening with respect to recrystallization as well as crystal deformation [2]. Whereas the matrix surrounds the major fraction of an applied load, the small additives hinder the motion of dislocations, and therefore, plastic deformation is restricted due to the tensile strengths [3–5]. Accordingly, sintering and phase decomposition in an inhomogeneous ceramic matrix through firing have a significant use for determining the manufacturing process in ancient ceramics and, furthermore, the quality of objects in the past. Generally, sintering is defined as a process that took place via phase transition, and makes most bulk ceramic components compact. An
important phase transformation involves crystallization of high-temperature phases between 900 and 1050 °C in ancient ceramic matrices (or earthenware) [6]. Due to the recrystallization process, the body of the ceramic tends to become more stable. The initial deformation through the phase–interphase area is important for early hardening in the structure [7]. The deformation proceeds by increasing the temperature until the structure is totally decomposed. Therefore, one can assume that we will see the last stage of deformation through microscopic observation. Sinter temperature is the temperature by means of which the grain boundaries have to be damaged in order to build a smelt or new recrystallization [3]. According to the thermodynamic properties of the material, by passing the stability area of a solid phase to the sintered phase, the ceramic matrix becomes more unstable because of changing the viscosity in the phase–interphase area, as well as increasing the surface enthalpy [1]. For this purpose, the ceramic pieces from 5000 bc from Tappeh Zaghe in Iran have been chosen for the analysis. The primary studies on the characterization of the samples were carried out in 2013 [8]. The archeological context is proved based on archeological documentation and indexing [9–11]. The aim of this study was to confirm and characterize the recrystallization process through partial sintering with respect to lattice diffusion in the mineral structure. The investigated ceramics are proved to have a black core in their macroscopic and microscopic profiles. Black cores in ancient ceramics occurred via fragmental and incomplete firing, which helped to find the best preferred mineralogical–phase deformation [12]. Indeed, it is possible to obtain a qualitative characterization of nanostructures within intergranular deformation, which were induced by transformation polymorphic structure before sintering, through high-resolution-microscopy methods [13,14].

This is a key point for the investigation of ancient potteries based on the observation of the exterior mineral boundaries for elucidating their sintering temperatures [15]. Using laser–scanning techniques, one can reconstruct the manufacturing strategy that was applied during the production maturity.

2. Materials and methods

The samples are from early excavation at the ancient site of Tappeh Zaghe, which was carried out by Negahban in 1970 [16]. The samples have until now been kept in the treasury of the Archeological Department of the University of Tehran, Tehran, Iran. The observation on the surface of the objects suggests some information about the texture of the ceramic pieces. As mentioned before, the ceramics are excellent in their quality and unique objects with smooth surfaces in form, and, in many cases, these pieces proved to have a red decoration on the surface (Fig. 1). They contain just three textural characteristics for consideration: the matrix, which is mostly inhomogeneous and surrounds the other crystalline constituents; the additives, which are dispersed or scattered in the matrix as tiny crystals with different geometry and grain size; and finally, the pores [17]. The pores occur in two different ways: the first path is via sintering due to the shrinkage of the matrix, and the second path is after cooling due to the rate of cooling of a ceramic’s matrix [3,18]. The color of the body tends to be yellowish beige, and the core of the samples in some cases proved to be dark (or black) due to the uncompleted firing process [12,19]. The dark color of the samples is not always based only on the incomplete firing, but also could occur with respect to the organic additives in the samples [20–22]. According to the very fine thickness of the objects, the investigated thin sections were prepared after gluing the surface of the objects on glass twice (Fig. 2).

The analysis of the crystalline–phase composition after firing was carried out by X-ray diffraction, using equipment from XPert Pro (PANalytical). The mineral phases were quantified using a Rietveld-based quantification routine with the XPert HighScore Plus software from PANalytical, and crystal patterns were chosen based on the International Center for Diffraction Data powder-diffraction file from the find It program. A number of corrections of various parameters were implemented, including the geometry of the crystal, preferred orientation, asymmetry, crystallographic axes, and scale factor. Polarization microscopy has been carried out on the thin sections of ceramic slices.
at suitable points using the atomic force microscopy (AFM) and piezo response-force-microscopy instrumentation from JEOL with supplementary WSxM 6.3 software. The point analyses were first identified by reflected light microscopy.

3. Results

3.1. Observation through polarized light microscope

The microscopic observation in all studied ceramics proved a layering structure based on their fragmented firing [19]. The most well-defined crystalline phases in the ceramics are observed on the external layer of the ceramics, and it seems that the external part had irregular firing or postponed heat transfer, in contrast to the matrix of the objects. The matrix of the body proved to have a regular sintered structure (Fig. 3A). Consequently, the outer layer of the pieces is not complimentarily sintered [23]. The mineral constituents within the outer layer are mostly well able to be interpreted. They consist of calcite, quartz, feldspars, plagioclase, and granitic rock fragments. Calcite was observed with its typical optical characteristic, and it seems that this layer has covered the ceramic body as slip. Calcites have been detected through high birefringence and good occurrences of cleavage in their texture (Fig. 3B). Calcites are the best phases for studying partial sintering, because they show the heat treatment that is needed for
decomposition of calcite to calcium oxide by ca. 800 °C [24]. Quartz is normally observed based on its high birefringence and undulatory extinction effect. The matrix of this layer is clayey and, due to the high porosity, seems to be less compacted (Fig. 3C). Plagioclases are interpreted based on their polysynthetic twinning after Carlsbad role [25] (Fig. 3D). Most high-temperature twinning, as well as pyro-technological new crystallizations, are observed in the core of the ceramic objects [26], and will be interpreted via ESEM images.

3.2. Crystalline-phase composition by X-ray diffraction

Selected diffractograms of ceramic samples illustrate all major crystalline phases based on their best preferred orientation in their powder pattern (Fig. 4). All of the minerals that are observed through the polarization microscope are also detectable due to the inorganic crystal-structure database powder-diffraction pattern. With respect to the thermodynamics of mineral occurrences, two groups of phases are observed; the first group is the low-temperature phases that were used as fillers or the minerals that were related to the raw materials (e.g., quartz, calcite, muscovite, and sanidine) [1,27,28]. The second group is the high-temperature phases that are produced via recrystallization and partial sintering (e.g., anorthite, diopside, gehlenite, and hematite) [29–32].

All of the crystalline phases are refined with respect to their crystallographic-pattern character. Profile fitting was applied to decompose the complicated powder pattern [33,34]. A profile function is fitted to the observed intensities. The goal is to obtain better peak parameters, completely describing the measured scan. A Kα1 profile is characterized by three parameters: peak position, net intensity, and full width at half maximum [35]. Additional parameters are the Kα2/Kα1 ratio and the background intensity. X’Pert HighScore utilizes the Pseudo–Voigt profile function, which is the weighted mean between a Lorentz and a Gauss function [36,37]. The fitting process is carried out with a goodness of fit of about 3.2 and the best preferred orientations of phases that are mentioned in Table 1.

A quantitative phase analysis can be performed on multiphase samples. The general scattering cross-section for Bragg scattering is proportional to N/V, where N is the number of unit cells contributing to the scattering and V is the unit cell volume [34]. The scale factor is then proportional to N/V.

As expected, the best present crystal is quartz with its very well-defined habit and structure in thin sections. Quartz is the foremost crystal that is observed in the external as well as internal layers of ceramics. Therefore, it appears with very sharp peaks and low full width at half maximum in a preferred orientation of about 2θ = 26°. Calcite, pyroxenes, gehlenite, and all possible secondary phases present with wide peaks that are randomly located above the background [1,38]. Plagioclases are refined very inflexibly due to the high asymmetry in their crystal structure. Hematite and muscovite overlapped each other mostly due to the close occurrences of preferred orientations in the diffractogram. Hematite can occur in a low-scale factor, and therefore, can be also the secondary hematite after weathering of iron-rich clay in exposure to humidity or acidic drainage, which was leached out of the iron from the crystal structure of the clay [39].

![Fig. 4. One of the ceramic piece’s diffractograms illustrating the crystalline phases in the matrix; otherwise, as filler. An = anorthite (CaAl2Si2O8); Cc = calcite (CaCO3); Di = diopside [CaMg(Si2O6)]; Geh = gehlenite [Ca2Al[AlSiO7]]; Hem = hematite (Fe2O3); Mus = muscovite, K[Al2[(OH)2]AlSi3O10]; Qz = quartz (SiO2); Sa = sanidine (KNaAlSi3O8).](image-url)
Table 1
Calculated crystalline phases in the body of the ceramics with respect to their inorganic crystal-structure database pattern and their best preferred orientation.

| ICSD pattern | Compound name | Best preferred orientation [2θ] | Scale factor | Chemical formula |
|--------------|---------------|---------------------------------|--------------|-----------------|
| 071835       | Diopside      | 29.822                          | 0.177        | (Ca 0.959 Ti 0.041) (Mg 0.987 Al 0.013) (Si2 AlO6) |
| 064957       | Sandine low   | 26.938                          | 0.076        | (K 86 Na 14) (AlSiO3) |
| 022022       | Anorthite     | 27.863                          | 0.155        | Ca (Al2 SiO5)   |
| 086453       | Gehlenite     | 31.435                          | 0.042        | Ca2 Al Si O8 (Al 1.22 Si 0.78 O 6.78) (O H) 0.22 |
| 088417       | Hornfelsite   | 33.243                          | 0.035        | Fe2O3           |
| 083849       | Quartz low    | 26.644                          | 0.987        | SiO2            |
| 010405       | Calcite, magnesia | 29.724                        | 0.065        | Mg 0.1 Ca 0.9 C O3 |
| 202261       | Muscovite 2:ITM:RG | 34.877                        | 0.159        | K Al3 Si3 O10 (O H)2 |

3.3. Characterization of texture and phases by environmental scanning electron microscopy–EDX

The samples are investigated with respect to their contrast in phase constituents as well as their vitreous character in the core, which is characterized through its typical sinter structure (Fig. 5). The difference among elemental distributions was observed based on two point analyses (Areas 1 and 2 in Fig. 5), which confirmed dominantly the enrichment of calcium in the external part (Area 2) in contrast to the core of the ceramic (Area 1).

Sinter structures are normally characterized by means of their viscose texture and bubbles that were produced from CO2 or SO3 evaporation [33] (Fig. 6A). Iron accumulations in the external layer of ceramics are present as a result of the coloring decoration on the surface due to the usage of red ochre in the ceramics. Normal sintering occurred in the entire grain boundaries (Fig. 6B). Normally, this kind of sinter structure is expected to form in a temperature range of >1200 °C, but in the ancient ceramics, it can also happen in a temperature range between 950 °C < T < 1050 °C [40,41]. Ceramic firing usually has a firing (or sintering) path, which depends on the oxidation or reduction reaction as follows [31]:

Dehydration (~100 °C) → loss of organic matter (~400 °C) → dehydroxylation (~600 °C) → carbonate decomposition (~750 °C) → recrystallization (~900 °C) → partial sintering (~1000 °C) → sintering (~1050 °C)

Quartz grain is easier to find within the thin section because, mostly, this was used as a filler or as inorganic nonplastic mineralogical additives in different grain sizes [40]. Quartz, plagioclase (mainly albite), calcite, and muscovite with definite crystal planes (0 0 1, 1 1 0) are the remaining phases from the raw material, whereas the other phases present have been formed during firing. The new crystalline phases that are rebuilt within the structure are pyroxene-type phases, such as augite or diopside (as detected also through X-ray diffraction). Augite and diopside are the last stages for high-temperature new recrystallization in the ceramic texture [23]. According to their formation as well as transition from other primary phases, these phases are very useful for detecting the partial sintering around their grain boundaries. The typical

Fig. 5. Sinter structure in ceramic matrix. The structure is viscous iron-rich muscovite behind augite newcrystallization in the matrix. Iron has a role as flux in these samples for decreasing the sinter temperature.
microstructure of noncontinuous vitrification in high calcareous clays is illustrated in Fig. 6C, while the core has an entirely different microstructure [42]. The microstructure consists of a noncontinuously vitrified surface and a high concentration of fine bloating pores. This kind of microstructure is typically produced by a low firing condition [43]. Sheet silicates, such as biotite or muscovite, show this transition effect from solid to liquid with clarity [6]. In a clayey matrix, this transition is also detectable due to its crystal-structure deformation by increasing heat (Fig. 6D).

3.4. AFM application in piezoresponse-force-microscopy mode for discovering the decomposition of grain boundaries through partial sintering

The main part of this study focused on the detection of deformations as well as any crystalline defects on the boundaries of constituent phases. With the application of atomic-force-microscopy methods in the nano-scale area, crystal deformations or defects around the external boundaries of the crystal structure can be illustrated [18]. Based on the recent works that have been carried out by Emamiet al. [44], some crystalline phases, such as sheet silicates and quartz, have been studied. With respect to their crystal structure, the important part of each crystal system of sheet silicate (mainly clay) is AlO$_6$octahedron. AFM scanning imaging in noncontact mode proved that the deformation of crystals began from the surfaces or layers perpendicular to the AlO$_6$octahedron (Fig. 7). Fig. 7 shows three different scans from one similar area in different magnifications of approximately 200 nm, 100 nm, and 32 nm, respectively; the left picture is the scan of topography, and the right side is a cohesive picture of the scanned area [18]. The topography picture clearly shows the layering structure of sheet silicate, but in the cohesive picture, it is clear to show the different cohesiveness based on transition conditions on the solid structure. Based on these investigations, it is possible to obtain a model for crystallization as well as crystal alteration in the phase-interface area toward the crystallographic C axes. The direct transition and high velocity of reaction throughout [001] suggest that AlO$_6$octahedron from the clay are being preserved during partial sintering [45]. Partial sintering happened for the first time by means of challenging along the viscosity changes between the plane, and was followed by a new crystallization phenomenon [18].
Surface characterization and partial smelting of the grain boundaries. This picture illustrates in situ atomic-force-microscope observations in RFM mode of sheet silicate with its plane structure in an average grain size from 200 nm to 32 nm, which shows the phase–interphase deformation due to the viscosity exchange in this crystal. The muscovite grain boundaries are not decomposed in a brittle manner, but elastic deformation is reported along the plane boundaries.

4. Discussion

Sintering is a well-known term in ceramic science. Ceramic materials are objects that must be sintered to achieve better physicochemical properties, and are thermodynamically proved to be metastable. Sintering has mostly been investigated as a mechanism, not a result. Archeological earthenware objects are interesting objects...
that consist of different mineralogical-phase constituents with respect to the different sinter temperatures due to kiln construction in antiquity [46]. Indeed, ceramic technology is the oldest human tradition, but the newest scientific knowledge, and therefore, the investigation of old objects can suggest better interpretations for the characterization of technical ceramic-manufacturing processes nowadays. Sintering is not a process that quickly happened; rather, it took place via partial smelting of the grain boundaries in the matrix. According to this point of view, sintering and partial smelting of the matrix must be studied together [2,30,47]. Sintering is discussed here as the result, and partial smelting as the process. In many cases were suggested about the good firing and sintering, whereas the heat-transfer process was not carried out completely. According to the crystalline-phase compositions and their decomposition, it will be of interest to explain the state of the objects as being in the partial smelting zone or the smelting zone. Investigations regarding the partial smelting state are of considerable interest, because, in this state, the matrix is exposed to maximum mass diffusion through the crystalline-phase decomposition [46,48,49]. Different samples have been studied by means of their application for characterization of sintered texture. The samples are investigated via AFM in order to characterize the grain boundaries and their defects through sintering via partial smelting. All of the samples are from 5100 bc, and they seem to have optimal firing because of the solidity of their bodies. Archeological objects are preferred objects because they were made from well-processed soil and clay from their original regions, and, furthermore, their manufacturing techniques are actually primitive, and therefore, lead to a better visibility of texture. By contrast, partial smelting of clay minerals causes a better adherence of texture. In the earthenware materials, mostly 2–3% of clay minerals were found, which are classified as the secondary mineralization [7]. Partial sintering is also more detectable through AFM on the grain boundaries that were decomposed and rebuilt. Pseudocrystalline of SiO2 is solved after 900 °C in small channels successively parallel to (001) plane. The external boundaries are changed by means of decreasing the volume and increasing the viscosity on the external surface of the crystal structures.

5. Conclusions

This investigation suggests that Zaghe-type potteries have been made by a sophisticated process that included fine mantel layer on the surface and, at the same time, notably sinter structure in the body. Identification of the know-how for processing and usage of raw materials fasten together for identifying a complicated puzzle of >5100 years. High-resolution microscopic investigations of ancient objects suggest not only the useful interpretation about the development of textural features of an antique object, but also expand the material characterization strategy nowadays. A recent study provided a more complete appreciation of the technology 7100 years ago, and approve to characterization of a phenomenon called “partial sintering” based on high-resolution laser application in materials-science research combined with archeology.

Based on the mineralogical–chemical investigation, the potteries in Zaghe divided themselves in two separate groups, due to the raw-material usage. The first group is the Zaghe type, which has been made by a clayey (and calcareous) rich matrix. The grain size in the matrix is very fine and dense. The second group was proved to manufacture by iron-rich raw material. To characterize the partial sintering, high-resolution-microscopy methods (AFM and ESEM) were applied for determining the grain boundary behavior in the phase–interphase area with respect to the viscosity exchange through high-temperature practice. According to the investigations, partial sintering is a reaction that would be controlled by different mineralogical parameters. In ceramic matrix, the SiO2/Al2O3 + FeO indicates the assessment of reaction from solid to sol–gel phases during the sintering process. All these oxides present mainly in the solid phases (such as gehlenite, anorthite, K-feldspars, and muscovite).

By contrast, partial smelting of clay minerals causes better adherence of texture. The surfaces of the standard Zaghe ceramics (5100 bc) proved significant, continuously covering the mantel layer (or slip; ca. 1 mm) of nonfired silica-rich slush. The mantel layer does not confirm to be fired because of hydrated calcite and the remains of volcanic stone fragments, such as plagioclase, feldspars, and muscovite. Indeed, this layer could be identified as one of the oldest slips for pottery-decorating process. This layer disappeared from the 4900 by the appearance of Cheshme-Hali type.

Conflicts of interest

The authors declared no conflicts of interest.

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