Journal of Microscopy and Ultrastructure 4 (2016) 11–19

Contents lists available at ScienceDirect

Journal of Microscopy and Ultrastructure

journal homepage: www.elsevier.com/locate/jmau

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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ARTICLE INFO

Article history:
Received 14 March 2015
Received in revised form 14 July 2015
Accepted 26 August 2015
Available online 6 September 2015

Keywords:
Atomic force microscopy
Crystal chemistry
Environmental scanning electron microscopy
Mineralogy
Partial sintering

ABSTRACT

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.

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

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http://dx.doi.org/10.1016/j.jmau.2015.08.003
2213-879X/

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).

Fig. 1. Investigated ceramic objects from the 5th millennium BC from Tappeh Zaghe with the typical red decoration on their surfaces.

The analysis of the crystalline-phase composition after firing was carried out by X-ray diffraction, using equipment from X'Pert Pro (PANalytical). The mineral phases were quantified using a Rietveld-based quantification routine with the X'Pert 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