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Strain-induced phase transformation behavior of stabilized zirconia ceramics studied via nanoindentation

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ABSTRACT

To study the tetragonal-to-monoclinic (T-M) phase transformation behavior under different strain rates and indentation depths, nanoindentation tests were performed on stabilized zirconia ceramics with Continuous Stiffness Measurements. The results indicate decreased phase transformation velocities at both lower and higher strain rates, but increased velocity under medium strain rate during loading. The phase transformation process is sensitive to $\dot{P}/P$ but the final volume fractions are almost identical (45%). Furthermore, most of the phase transformation is completed during a short initial time followed by slight linear increase of the M-phase volume fraction with holding time. The phase transformation continuously slowed with increasing indentation depth when indented with a constant strain rate.

1. Introduction

Due to stress-induced tetragonal-to-monoclinic (T-M) phase transformation in stabilized zirconia ceramics, the application of zirconia ceramics in prosthetic dentistry is highly desirable for their excellent chemical durability, wear resistance, and biocompatibility (Abdur-Rasheed et al., 2014a; Peng et al., 2017). The transformation leads to high mechanical toughness and strength, attributed to the effect of transformation-toughening associated with the martensitic tetragonal to monoclinic phase transformation (Hin et al., 2004; Bighetti et al., 2014), which extends the application of zirconia ceramics from bearing components to biomedical protheses and others uses for extreme conditions (Gaillard et al., 2009; Choi et al., 2005).

Many authors have studied the transformation behavior of stabilized zirconia ceramics using various methods and studying different conditions (Patrick et al., 2002; Mahmood et al., 2013; Hin et al., 2004; Bighetti et al., 2014; Choi et al., 2005; Chevalier et al., 2009; Jimínez-Píqué et al., 2000; Fadda et al., 2009; Rauchsa et al., 2002). The T-M phase transformation which has been evidenced by numerous transmission electron microscopy studies is martensitic (Hayakawa et al., 1989; Calvié et al., 2013). The generation of solid-state phase transformation is mainly motivated by force and thermal. The phase constitutions of zirconia depend on the actual state of monocrystals versus polycrystalline aggregates as well as purity (Fadda et al., 2009). Consequently, the stabilized zirconia cannot generate transformation if zirconia is not affected by stress, ignoring the influence of service environment. The transformation can be affected by several factors, such as the magnitude of load, loading way, stress route, and loading rates. Therefore, stress or strain induced T-M transformation of zirconia has attracted extensive attention among researchers.

Given the higher resolution measurements, nanoindentation technique is well suited to measure the near-surface mechanical properties of flat samples, such as hardness and Young's modulus at a nano-scale (Maerten et al., 2013; Gong et al., 2004; Hallmann et al., 2014). Oliver and Pharr (1992) developed one of the widely used methods for the determination of the contact area and properties calculation. The Oliver-Pharr method (O & P model) has been successfully used for analyzing the nanoindentation data measured on various ceramic materials (Gong et al., 2014; Guicciardi et al., 2007a, 2007b; Zhang et al., 2012; Tiwari et al., 2014; Liu et al., 2015; Thomas et al., 2015). Several nanomechanical studies have been carried out to investigate the effect of grain size (Guicciardi et al., 2006), ageing (Guicciardi et al., 2006, 2007a, 2007b; Catledge et al., 2003), indentation size effect (Shao et al., 2013) and crystallographic orientation (Gaillard et al., 2009) on the mechanical behavior of zirconia. The measured mechanical properties are strongly influenced by the loading mode of indentation (Guicciardi et al., 2006; Morales et al., 2010). Effect of loading rate on the mechanical behaviors of zirconia was investigated using nanoindentation and in situ scanning probe imaging techniques, and the results showed plastic deformation without fracture at all loading rates (Abdur-Rasheed et al., 2014b). In order to explore the mechanisms behind T-M phase transformation induced by

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intergranular microcracking and the effect of variant martensitic strain accommodation on the formation of microstructural and topological patterning in zirconia, the phase-field technique and model was developed (Zhu et al., 2017; Mahmood et al., 2013). However, most of these studies focused on the phase transformation mechanism and the effect on material properties, the corresponding degree or level index of phase transformation has not been systematically studied at the submicron scale.

Based on Continuous Stiffness Measurement (CSM) proposed by Oliver and Pharr (Pethica et al., 1987; Pharr et al., 1992), hardness and elastic modulus can be continuously obtained with indention depth. Furthermore, mechanical properties of zirconia ceramics show a strong dependence on phase constitutions and compositions, as well as grain size and distributions. But the elastic modulus is a response to atomic bonding strength of materials, which is insensitive to the grain size and distributions of materials. The general decrease of the Young's modulus with the increase of the ageing time was again due to the increase of monoclinic phase content (Guicciardi et al., 2007a, 2007b). Therefore, the variations of elastic modulus are considered to be originated mainly from the atomic arrangement caused by the phase transformation. The elastic modulus can be taken as an indicator of the tendency of phase transformation for the same material despite of the complexity of the state of stress and strain in the region of the indenter. Consequently, the strain induced phase transformation during indentation can be qualitatively and quantitatively presented via the nanoindentation method based on the CSM method.

In this study, T-M phase transformation of stabilized zirconia ceramics was studied via nanoindentation tests under different strain rates and indentation depths based on CSM. Elastic modulus and M-phase volume fraction during loading and holding were calculated according to the O & P model to reveal any correlations between strain rate, strain, and phase transformation.

2. Strain-induced phase transformation

T-M phase transformation has several features, such as lack of diffusion, variable temperature, surface relief, reversible transformation, and shearing strain (Hsu, 1995), which is consistent with the characteristics of martensitic transition. Treating T-M phase transformations as martensitic phase transformations has been widely accepted (Hin et al., 2004; Bighetti et al., 2014; Choi et al., 2005; Chevalier et al., 2009; Jiménez-Píqué et al., 2000; Fadda et al., 2009). Thus, the T-M phase transformation mechanism can be interpreted as martensitic phase transformation.

Based on the Reuss scheme, the mixture modulus E_{mt} of zirconia with multiphase complex structure is obtained and expressed as (Auricchio et al., 1997):

$$\frac{1}{E_{mt}} = \frac{1}{E_t}(1 - z) + \frac{1}{E_m}z \tag{1}$$

where E_m and E_t are monoclinic and tetragonal elastic modulus, respectively, and z is the monoclinic phase volume fraction.

The strain area is irregular and heterogeneous for the complex state of stress and strain in the region of the indenter, revealed by material survey via nanoindentation tests. This reveals an irregular and inhomogeneous zone affected by stress or strain of indentation. In the vicinity of indentations, the extent of the transformed phase decreases almost linearly with distance from the center of the indent (Chien et al., 1998). For this study, it is assumed that the M-phase volume fraction can be quantified as a percentage of double-phase structure in the stress or strain affected zone, despite of the zone volume increasing with the indentation depth during indentation. Furthermore, it is considered that the phase transformation generated M-phase was randomly oriented and statistically distributed within the matrix of the tetragonal phase. This leads to a simplification for phase transformation and facilitates a convenient analytical solution for fundamental relations of the elastic modulus-transformation.

The M-phase volume fraction z can be calculated from *Eq.* (1) as:

$$z = \frac{(E_t - E_{mt})E_m}{(E_t - E_m)E_{mt}} \times 100\% \tag{2}$$

In initial state without external stress, the M-phase volume fraction can be calculated via the following formula based on XRD patterns (Garvie and Nicholson, 1972):

$$Z_{m0} = \frac{I_m(111) + I_m(11\bar{1})}{I_t(111) + I_m(111) + I_m(11\bar{1})} \times 100\% \tag{3}$$

where $I_m(111)$ and $I_m(11\bar{1})$ represent the intensity of the monoclinic peaks ($2\theta = 28^\circ$ and $2\theta = 31.2^\circ$, respectively) and $I_t(111)$ indicates the intensity of the respective tetragonal peak ($2\theta = 30^\circ$) (Guilardi et al., 2017).

Because the mixture modulus E_{MT} of zirconia ceramics can be continuously obtained from nanoindentation via CSM, additionally both M and T phase elastic moduli have been addressed (Fadda et al., 2009; Fogaing et al., 2006; Erich et al., 1998). The applicability of *Eqs.* (1) and (2) can be validated via *Eq.* (3) based on XRD patterns during the initial state, as well as via M-phase volume fraction, calculated in real-time during indentation via *Eq.* (2).

3. Material and testing

3.1. Materials

The materials used in this study were a commercial zirconia ceramic (Ce-TZP) (stabilized with 2.5 mol% CeO_2) monoliths acquired in powder form and then sintered, produced by Baotou Institute of Innovation, Peking University. Prior to nanoindentation, the specimen surface was polished with a polishing slurry.

3.2. XRD tests

XRD analysis was performed as a complementary helpful technique to determine the phase constitution and monoclinic phase volume fraction according to Eq. (3) during the initial state. The XRD analysis was performed using an X-ray diffractometer (Bruker AXS D8 Discover, Germany) with a CuKα radiation.

3.3. Nanoindentation tests

Nanoindentation tests were carried out using the Nano-indenter G200 test system (Agilent Technologies) with force and displacement resolutions of 50 nN and 0.01 nm, respectively. A triangular pyramid Berkovich diamond indenter was employed. Fused silica was indented firstly to calibrate the accuracy of the testing system. The constant indentation strain rate condition was realized by performing load-controlled indentations with a constant value of loading rate/load ($\dot{P}/P$) for loading (Oliver et al., 1992). All indentation tests in this study were carried out under five different strain rates of 0.01, 0.05, 0.1, 0.2, and 0.3 s^{-1} and all the indentation tests were repeated 3 times. As soon as the maximum indentation depth was achieved, the indenter remained at the corresponding peak load for 200 s before withdrawal from the specimen to obtain the transformation behavior of zirconia. Additionally, the elastic modulus and hardness were continuously obtained during loading based on the CSM technique.

For constant strain rate $\dot{P}/P = C$, the load–time curve during loading is shown in Fig. 1. The load increases exponentially related to time during loading, and remains constant during holding time after reaching the maximum P_{max}, and unloading to $0.1P_{max}$ before correcting for thermal drift. Machine compliance and thermal drift correction are automatic.

In the O & P model (Oliver et al., 1992), the contact area A_c, is