



INFLUENCE OF THERMAL TREATMENT ON ZIRCONIA POWDER

Livia GHEORGHIES

"Dunărea de Jos" University of Galati, Faculty of Materials Engineering and Environment,
111, Domnească Street, RO-800201, Galati, Romania
email: cgheorg@ugal.ro

ABSTRACT

Zirconia powder in amorphous state was prepared by electrolytic deposition method (ELD) and then it was subjected to a thermal treatment according to a typical diagram. The structural changes in zirconia powder induced by thermal treatment have been pointed out by X-Ray diffraction (XRD), thermogravimetric analysis (TGA) and differential thermoanalysis (DTA) techniques. During thermal treatment, XRD patterns and DTA curves showed the presence of a mixture of two crystalline phases well-formed at approximately 400°C and a transformation of the type tetragonal-monoclinic ($t \rightarrow m$) at approximately 600°C. In situ XRD study allowed establishing the growth kinetics of crystalline phases. Using experimental maximum intensities, $H_{(hkl)}$ and integral intensities, $I_{(hkl)}$, of XRD peaks, the volume fractions, V_m and V_t , of m and t phases, respectively, present in a polymorphic mixture were calculated.

KEYWORDS: zirconia, powder, temperature, structure

1. Introduction

Zirconia is an oxide ceramic with chemical formula ZrO_2 that has attracted the interest of researchers mainly due to useful properties in practical applications such as thermal stability, thermal shock resistance and corrosion resistance. This oxide ceramic is used in catalysis technique and electronics as dielectric and piezoelectric material. Ceramic materials based on zirconia have many applications due to their many qualities such as heat resistance, high strength and hardness, low thermal conductivity, and ionic conductivity at high temperatures [1-2]. These materials fabricated by different techniques are used as tribological protections, thermal barriers for engine, and bioinert coatings in the medical field [3-5]. Often the ways of obtaining and processing powder influence the properties of ceramics.

ELD is among the many techniques used to obtain powder materials. Using aqueous or organic solutions, this method is often preferred for the preparation of powders due to primarily relatively simple technique which takes place at normal temperature and pressure, possibility of application to industrial scale and automation. The electrolytically obtained powders have a high purity and their microstructure can be controlled and managed by

monitoring operating parameters such as electrolyte type, its concentration and pH, and other process variables, i.e. voltage, electric current, temperature, speed of reaction.

Under normal conditions, zirconia exists in three polymorphic forms in equilibrium state for different temperature, T , according to the Joint Committee on Powder Diffraction Standards (JCPDS) [6]: monoclinic (m) $T < 1205^\circ\text{C}$ (JCPDS: 37 – 1484), tetragonal (t) $1075^\circ\text{C} < T < 2377^\circ\text{C}$ (JCPDS : 50 – 1089) and cubic (c) $2377^\circ\text{C} < T < 2680^\circ\text{C}$ (melting point) (JCPDS : 51 – 1149). Zirconia forms of higher symmetry have properties very often preferable to the ones of monoclinic form so they are stabilized in various ways. The temperature at which the tetragonal to cubic transformation occurs can be lowered, by the addition of some solutes such as MgO , CaO , Y_2O_3 . The presence of tetragonal zirconia as dispersed phase determines the increasing of the fracture strength, toughness and hardness of oxides as well as nonoxides ceramics [7].

Due to its high melting point, zirconia is an attractive refractory material. However, $t \rightarrow m$ transformation is accompanied by an increase in volume that causes disintegration of powder during cooling process [8]. The knowledge of the $t \leftrightarrow m$ transformation mechanism determined by the influence of thermal processes is very important in

the industrial applications. In some circumstances, the tetragonal phase is present in addition to the monoclinic phase at room temperature (RT). This is the subject of research of many scientific papers.

According to them, the reason for the formation of this high temperature phase at RT can be: presence of anionic impurities or other defects in the lattice as adsorbed oxygen [9]; residual stresses [10]; minimum surface energy [11]; lattice defects as oxygen vacancies or water vapours [12].

The $m \rightarrow t$ phase transformation can be controlled by nucleation mechanism that is almost nonexistent at RT but can be activated mechanically or thermally [13].

The purpose of this paper is to study of effects the thermal treatment on the phase transformations undergone by amorphous zirconia obtained by ELD from an aqueous electrolyte.

A qualitative and quantitative analysis on identification for the crystalline phase of zirconia was conducted using XRD, TGA, and DTA methods.

2. Experimental procedure

Amorphous zirconia powder was prepared by ELD from an aqueous solution of $ZrO(NO_3)_2$ (Merck, p.a. grade) on a graphite cathode with spectral purity [14]. The resulting powder was heat treated at different temperatures from RT to 800°C.

Structural investigation was made by a DRON 3 X-ray diffraction instrument equipped with a high temperature oven-chamber using $CuK\alpha$ X-ray with the wavelength $\lambda=1,5417 \text{ \AA}$, at a voltage of 36 kV and a current of 20 mA.

During the experiments, temperature was controlled with a Pt-Pt-Rh (10%) electronic thermocouple having an accuracy of $\pm 1^\circ C$. The sample was prepared by pressing the starting compound into a tantalum grid. The scanning angle, 2θ , was varied from 26° to 34° with a detection step of 0.02° while the temperature was increased. In order to eliminate any effects of texture during the XRD analysis, the sample was rotated in a plane parallel to the axis of the goniometer. The international diffraction data base of JCPDS has been used to identify the crystalline phases.

In order to elucidate the changes in physical properties of zirconia powder as function of temperature, simultaneous measurement of TGA and DTA were performed by a derivatograph of the system F.Paulik, J.Paulik, L. Erdey (MOM, Budapest, Hungary).

The experiments were carried out in open crucible, with a heating rate of $20^\circ C/\text{minute}$ and using alumina calcined at $1400^\circ C$ as standard material.

3. Results and discussions

The crystal structure and phase composition of the resulting zirconia powder were investigated by XRD. Figure 1 shows the XRD patterns of the powder electrodeposited on the graphite electrode indicating the existence only of the typical graphite peak and none of the distinctive peaks of zirconia because this is amorphous. In order to characterize and identify the phase transformations caused by thermal treatment, the amorphous powder was removed from the graphite electrode and pressed into a sample tantalum holder which was put in the high temperature oven-chamber.

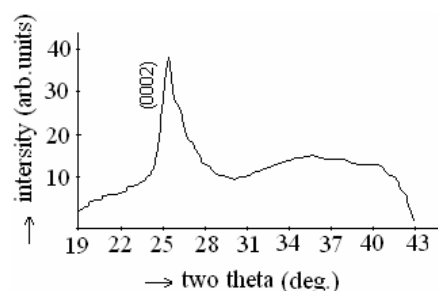


Fig. 1. XRD pattern of amorphous zirconia electrodeposited on graphite electrode

The heat treatment was performed at the different temperature in air or in argon atmosphere with the maintaining time of one hour and cooling together furnace. The evolution of the XRD patterns for different temperatures is shown in Figure 2. The appearance and development of (hkl) zirconia characteristic peaks with increasing temperature are pointed out.

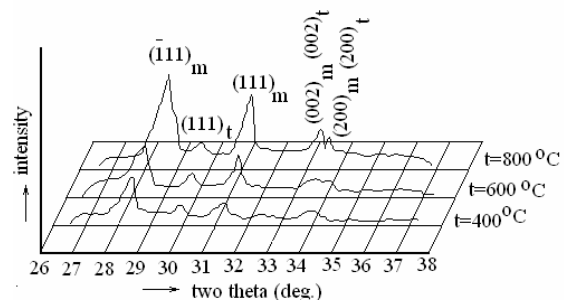


Fig. 2. XRD patterns of thermally treated zirconia powder

Only around $600^\circ C$, m and t phases are well formed and their $(200)_m$, $(200)_t$, $(002)_m$, $(002)_t$ peaks are clearly distinct. Consequently to calculate the volume fractions of the two phases, the $(111)_t$, $(111)_m$ and $(\bar{1}\bar{1}\bar{1})_m$ well-formed peaks were chosen.

Using experimental maximum intensities, $H_{(hkl)}$ and integral intensities, $I_{(hkl)}$, of these peaks, the volume fraction, V_m , of monoclinic phase present in a polymorphic mixture was calculated [15]:

$$V_m = \frac{P \cdot X_m}{1 + (P-1)X_m} \quad (1)$$

where

$$P = \frac{H_{(111)_t}}{H_{(\bar{1}\bar{1}\bar{1})_m} + H_{(111)_m}} \quad (2)$$

and

$$X_m = \frac{I_{(\bar{1}\bar{1}\bar{1})_m} + I_{(111)_m}}{I_{(\bar{1}\bar{1}\bar{1})_m} + I_{(111)_m} + I_{(111)_t}} \quad (3)$$

The data presented in the table 1 show that the volume fractions of the two phases, V_m and V_t , respectively, increase with temperature, but the former exceeds the latter.

Table 1. Volumetric fractions of zirconia phases

Sample	T	Atmosphere	V_m	V_t
	[°C]			
1	400	air	85	15
2	600	air	92	8
3	800	air	97	3
4	800	argon	97	3

In situ crystallization study requires fast collection of data at high temperatures. Such measurements were performed during both the heating and the cooling processes.

The heating was fast up to 400°C and slowly continued with a speed of 20°C/min up to 804°C. During heating, the X-ray detector scans were fast with a speed of 8°C/min and the direction of rotation of the goniometer was changed manually. One change requested 12 seconds and during which time the temperature rose by 4°C.

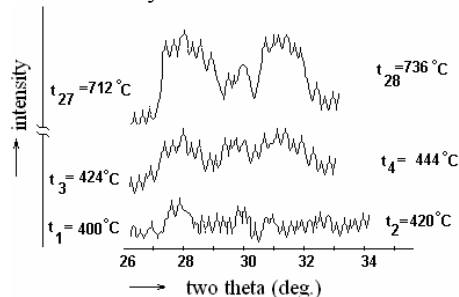


Fig. 3. In situ XRD patterns for different temperature ranges

The entire temperature range was covered in 1224 seconds when 17 scans were performed, seven

of them in counter-clockwise and the rest in reverse. Some of the obtained diffraction patterns are shown in Figure 3. Left and right values represent the starting and ending temperatures of the sample during scanning process.

The analysis of XRD patterns allowed establishing the growth kinetics of crystalline phases, i.e. development of mosaic blocks. The aspect of two experimental curves allows having an overview of the growth kinetics of the crystalline phases from amorphous powder as presented in Figure 4. The figure shows the existence of the two crystalline phases and their stabilization tendency after the temperature reached 804°C, during the heating process, the goniometer being fixed in specific angular positions to receive t and m phase peaks respectively.

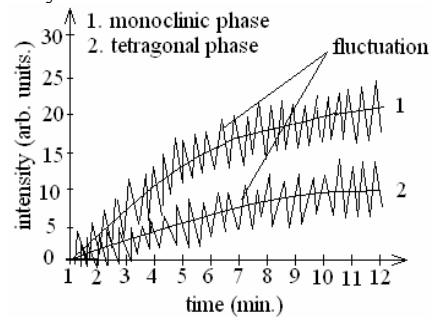


Fig. 4. Kinetics curves of crystalline phases

The cooling with a speed of 20°C/min from 804°C to RT was also conducted. Some XRD patterns presented in Figure 5 reveal that the tetragonal phase is stable to near about 400°C and then it was converted in the monoclinic form. Left and right values represent the starting and ending temperatures of the sample during the scanning process. Compared to the heating stage, kinetics is altered so that transformations occurred faster and at lower temperatures.

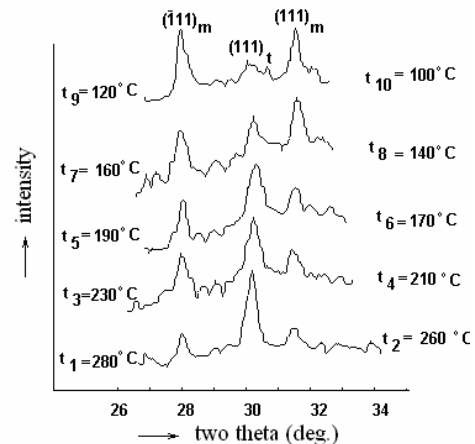


Fig. 5. XRD patterns of powder zirconia obtained at quickly scanning

The TGA and DTA data on zirconia powder are presented in Figure 6. A significant mass loss appeared at 150°C can be attributed to removal of water. It is accompanied at DTA curve by a low endothermic peak determined probably by the release of the volatile compounds. At approximately 400°C the well-formed exothermic peak corresponds to the crystallization of amorphous zirconia and the next lower peak appeared at approximately 600°C is determined by the $t \rightarrow m$ phase transition process confirmed also by XRD [16].

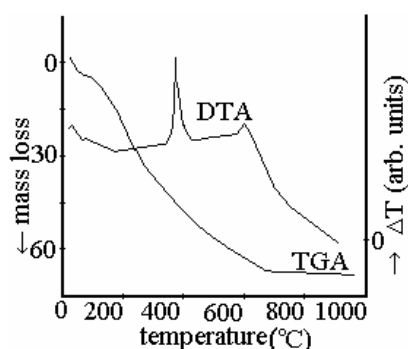


Fig. 6. TGA and DTA curves

4. Conclusions

Zirconia obtained by ELD is amorphous at RT and crystallizes after heating at about 400°C and the $t \rightarrow m$ allotropic transformation occurs at about 600°C. During the heating process of the electrodeposited zirconia powder, the volume fraction of the m phase exceeds the t one. Crystallization kinetics of zirconia powder can be determined by in situ XRD studies

over time following the changes of maximum or integral intensity of the diffraction peaks.

Modern XRD instruments equipped with suitable software permit the improving of the pattern quality and reduction of the data acquisition time, making this a more powerful technique.

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