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# Influence of Ar-ion implantation on the structural and mechanical properties of zirconia as studied by Raman spectroscopy and nanoindentation techniques

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ABSTRACT

In this study, structural and nanomechanical properties of zirconia polymorphs induced by ion irradiation were investigated by means of Raman spectroscopy and nanoindentation techniques. The zirconia layer have been produced by high temperature oxidation of pure zirconium at 600 °C for 5 h at normal atmospheric pressure. In order to distinguish between the internal and external parts of zirconia, the spherical metallographic sections have been prepared. The samples were irradiated at room temperature with 150 keV $Ar^+$ ions at fluences ranging from $1 \times 10^{15}$ to $1 \times 10^{17}$ ions/cm$^2$. The main objective of this study was to distinguish and confirm different structural and mechanical properties between the interface layer and fully developed scale in the internal/external part of the oxide. Conducted studies suggest that increasing ion fluence impacts Raman bands positions (especially characteristic for tetragonal phase) and increases the nanohardness and Young's modulus of individual phases. This phenomenon has been examined from the point of view of stress-induced hardening effect and classical monoclinic → tetragonal ($m \rightarrow t$) martensitic phase transformation.


## 1. Introduction

Due to its remarkable mechanical properties, resistance to corrosion and almost complete transparency to neutrons, zirconium and zirconium based alloys are very attractive for nuclear industry. For this reason, reported physical, mechanical and chemical properties of Zr-based materials allow to consider them as a future components used in next generation nuclear reactors [1]. Some designs such as: PWR (Pressurized Water Reactor) or BWR (Boiling Water Reactor) assume operating temperature exceeding 300–400 °C. These conditions cause severe oxidation process and deterioration of initial properties of the component [2]. It has been proven that high temperature oxidation of zirconium leads to the formation of tetragonal and monoclinic phases [3]. The tetragonal phase is preferentially located in the proximity of metal/oxide interface [4,5]. This assumption has been supported by Raman spectroscopy studies and by electrochemical impedance spectroscopy [6,7].

In addition to the classical oxidation effects, zirconium components are irradiated by fast neutrons. At the same time, fast neutrons are known to be responsible for corrosion resistance reduction and modification of the mechanical properties of the material. Therefore, comprehensive studies aiming to understand functional properties of irradiated materials are badly needed. However, neutron irradiation activates material, making its analysis very difficult (necessity to use dedicated Hot Cell laboratories). The best way to simulate the influence of the neutrons on the material expected to be used in radiative environment is ion irradiation. This technique allows one to study the material properties in a much easier way than by placing it into nuclear reactor and Hot Cell Laboratory afterwards.

Numerous studies have been performed on cubic (YSZ) single- [8] and polycrystals [9–11]. Moreover, Simeone et al. [12,13] studied mechanism of $m \rightarrow t$ phase transition induced by irradiation. The studies have been performed on monoclinic nano-powders. Despite considerable amount of work, this topic has not been fully understood yet. Among other problems, it is of prime interest to describe the mechanical properties of oxidized zirconium upon irradiation, and to assess nanomechanical properties of various phases formed during high temperature oxidation. Finally, the stress hardening effect should be always taken into account during structural and mechanical analysis.

Among different available techniques and measurement methodologies, recent progress in nanoindentation method allows one to assume that this is the most appropriate technique for small volume testing [14,15,30]. Despite many requirements, such as: (i) high quality surface, (ii) tip sharpness and frequent Diamond Area Function DAF checking, (iii) indentation size effect (ISS) and (iv) difficulty in measurement of

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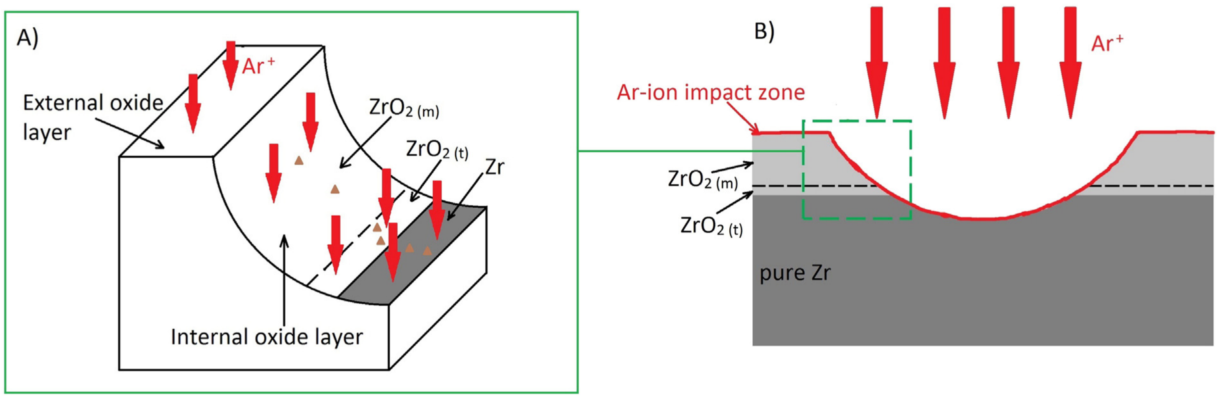


**Fig. 1.** A) Schematic 3D representation of the studied specimen: metallic substrate depicted as (Zr), inner oxide scale consisting from tetragonal and monoclinic phases depicted respectively as $ZrO_{2(t)}$ and $ZrO_{2(m)}$ and external part of the oxide. Red arrows indicate direction of the Ar-ion implantation into the material, small triangles represent spots where nanoindentation and Raman spectroscopy measurements took place. B) Spherical cross-section of the studied zone in 2D.

irradiated thin layers without response of the sample bulk, tremendous progress has been achieved [16,17]. In addition, it has been proved that nanomechanical properties of ion irradiated layer can be correlated with structural studies, such as GIXRD [18] and Raman spectroscopy technique. Therefore, one can conclude that reported in this paper results, open new paradigm for small volume investigations of ion implanted materials in the future.

In this study, the effect of room temperature ion irradiation on structural and nanomechanical properties of zirconium/zirconia system were studied by using Raman spectroscopy and nanoindentation techniques. Prior to irradiation, samples were oxidized at 600 °C for 5 h at normal atmospheric pressure. Afterwards, the spherical metallographic polishing technique have been applied. Radiation damage has been simulated by using 150 keV $Ar^+$ ions at fluences ranging from $1 \times 10^{15}$ to $1 \times 10^{17}$ ions/cm$^2$. Nanomechanical properties (hardness and Young's modulus) of zirconia phases were analysed. SRIM computer code has been used to evaluate the damage level of irradiated layer. Raman spectroscopy technique was used to investigate impact of ion implantation process of characteristic for monoclinic and tetragonal phases Raman bands. The mechanism of stress induced hardening of Ar-irradiated zirconium/zirconia system at room temperature and possible $m \rightarrow t$ phase transition were discussed. An attempt to distinguish between mechanical properties of internal oxide layer and metal/oxide interface, i.e. between regions rich in monoclinic and tetragonal phases, by comparing their mechanical response was presented. Reported mechanical studies are in full accordance with structural investigations conducted by means of Raman spectroscopy technique. It should be emphasized that according to authors knowledge, reported herein research is one of the first in this domain and opens new possibilities for future mechanical and structural comparative studies.

## 2. Experimental Details

Pure zirconium coupons (purity 99,2%) provided by GoodFellow Cambridge Company Ltd. Laboratory were used in the experiments. The zirconium specimens with dimensions 10 × 10 mm were cut from a 0.5 mm sheet of zirconium plates. In order to eliminate the internal stress created during industrial preparation, samples were heat-treated at 600 °C for 1 h before the experiments. Afterwards, samples were polished using sand paper ranging from 320× to 2000× gradation. After polishing, the specimens were cleaned with distilled water and ethanol. Finally, in order to develop sufficient oxide layer, the specimens were heated in the high temperature furnace at 600 °C, for 5 h at normal atmosphere (i.e. pressure 1013.25 mbar and standard atmosphere composition – ~78% N, ~21% $O_2$ and ~1% Ar). After oxidation, sixteen spherical abrasions (four for each irradiation fluence) were made by using Tribotechnic Calotester. In this method the abrasions are made by the spinning ball with 20 mm diameter which is covered with 1 μm diamond suspension. Drilling of the spherically shaped crater was carried out for about 30 min with rotational ball speed of 200 rpm. During the experiment, the spinning ball rests on the specimen and the clamping force depends on the size (weight) of the ball. In order to avoid overheating of the sample and/or to deep drilling, verification of the test advancement were performed every 3 min by standard optical microscope. Presented methodology allows one to reveal both, external oxide layer, the metal/oxide interface and zirconium substrate (see Figs. 1–3). A 3D scheme showing experimental geometry with above mentioned regions and spots (grey triangles) where Raman spectroscopy and nanoindentation tests were performed is presented in Fig. 1A). Afterwards, basing on the Eqs. (1)–(3), total oxide thickness has been estimated to be close to 4.5 μm. The calculations were repeated in 4 different 'craters' with measurement error of ±0.35 μm. One must remember that the layer thickness estimated by using this technique may be burden relatively large mistake due to considerable errors caused by poor quality of the images made with optical microscope. However, this calculation is in accordance with previously reported thermo-gravimetric studies [19]. Fig. 1B) presents the schematic representation of the spherical cross section and distinction into zones with high content of tetragonal and monoclinic zirconia phases.

In order to calculate the thickness of the zirconia, the ball/plan calculation model was implemented. In this model we assume that the ball is in the interaction with perfectly flat surface (see Fig. 2). If we take *P* as the total depth of the crater, *s* as the depth of penetration in the substrate and *c* as the thickness of the oxide layer, the equation can be

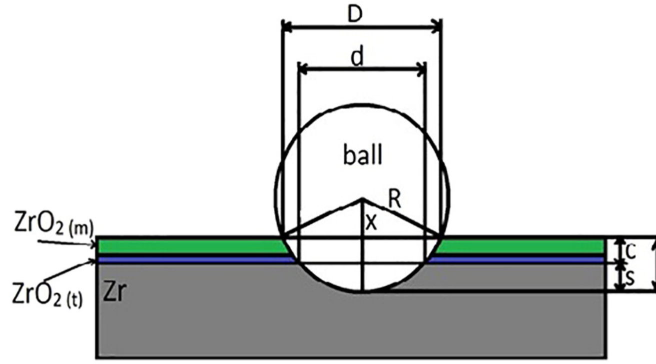


**Fig. 2.** Model representation of the spherical cross section experiment. Depicted dependencies allow to calculate the thickness of the oxide scale.