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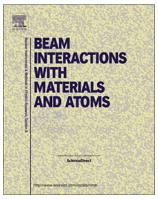

Nanoindentation study of irradiation and temperature effects in yttria-stabilized zirconia

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ABSTRACT

In the present study, the detailed evaluation of nanomechanical properties in terms of hardness and Young's modulus of irradiated polycrystalline YSZ pellets were studied using the nanoindentation technique. The samples were irradiated at room temperature with 150 keV Ar-ions to a fluences of 1×10^{14} and 1×10^{15} ions/cm^2 (i.e. before bubble formation), which correspond to a peak damage of 0.12 and 1.2 dpa respectively. Substantial improvement of mechanical properties related to the creation of both radiation defects and residual stress in the implanted surface layer were observed. Additionally, *in-situ* high temperature nanomechanical investigation of pristine YSZ pellet was conducted. A significant decrease of nanomechanical properties was observed with increasing temperature.

1. Introduction

Yttria (Y_2O_3) stabilized zirconia (ZrO_2, YSZ) is one of the most widely tested materials dedicated to future nuclear applications [1–3]. Outstanding mechanical properties and high radiation damage tolerance makes this material the strongest candidate to be used in the future ceramic-based inert matrix nuclear fuels [4] and nuclear waste systems [5]. Abundant amount of experiments aiming to study radiation induced microstructural evolution have been performed using X-ray diffraction, transmission electron microscopy, Rutherford backscattering spectroscopy/channeling, Raman spectroscopy, photoluminescence and atomic force microscopy [6–8]. However, a substantial research concerning nanomechanical properties of single and/or polycrystals has not been performed [9,10]. Additionally, mechanical parameters of YSZ have been poorly tested *in-situ* at high temperatures. It should be pointed out that material properties are likely to undergo changes in high temperature (HT) environment, and it is therefore of prime importance to perform experimental studies to collect the data on YSZ behavior at high temperatures. The aim of the present study is to contribute in filling this gap.

In this paper, nanomechanical properties of ion irradiated YSZ were investigated. Polycrystalline pellets were irradiated at room temperature with Ar^+ ion with fluences up to 1×10^{14} and 1×10^{15} ion/cm^{-2}. In order to investigate the mechanical properties of modified layer without significant contribution of the unirradiated bulk material, nanoindentation experiments were performed using forces that resulted in an indentation depth of 100–150 nm, i.e. roughly half of the projected range of ions calculated with the SRIM code [11]. Afterwards, the mechanical properties of polycrystalline samples were compared with literature data [2,3]. As reported by Menvie Bekale et al. [2], a strengthening of YSZ is associated with residual compressive stress induced by the ion irradiation in the modified layer. However, these studies concern high-energy ion irradiation. Therefore, the goal of this research was to verify if similar or the same effects occurs during low-energy ion irradiation, i.e. damage production in the elastic collision regime.

In the second part of this work, one of the first HT measurements of zirconia nanomechanical properties (at 200 °C), implementing classical nanoindentation test and the Load Partial Unload mode are presented. In order to conduct correct nanomechanical analysis at high temperature, one must control the basic characteristics of the equipment. As reported in the literature [12], the extension of nanoindentation technique to HT measurement is a relatively new possibility. According to Wheeler et al. [12], until the end of 2014, less than 150 scientific works were published addressing the topic of HT nanoindentation. One of the reasons of such a poor knowledge are problems occurring during the measurement, such as: thermal drift, contact between sample and indenter, thermal expansion of the sample, sample and indenter

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oxidation etc… NCBJ system (Micro Materials Ltd.) allow to test samples up to 750 °C. In this paper, measurements performed at 200 °C are aimed at checking the basic characteristics of the equipment and give one of the first insights in the HT mechanical data of YSZ. This work is a part of much broader research aiming to elucidate the mechanical properties of materials subjected to high temperatures and radiation damage.

2. Experimental

The samples used in this study are commercial GoodFellow Cambridge Limited polycrystalline zirconia fully stabilized with 5 mol% Y_20_3 with size of 15 × 15 × 1 mm. Roughness of the samples were measured using Hommelwarke LV-50 device. The test have been performed on 1 mm distance and repeated 5 times resulting with $R_a \approx 40$ nm (measurement error 15%). Studied samples were irradiated at room temperature with 150 keV Ar^+ ions. In order to minimize target heating the ion current during irradiation did not exceed 0.3 W/cm^{-2} (i.e. flux of ions $\sim 1 \times 10^{13}$ cm^{-2} sec^{-1}). The mean projected range of Ar^+ particles has been calculated with SRIM calculations [11], and it is 200 nm. Nanomechanical experiments were performed using a Micro Materials indentation system. Berkovitch shaped diamond and cBN indenters were used for room and high temperature measurements, respectively. High temperature investigation was performed at 200 °C in argon atmosphere (to prevent indenter from oxidation). Nanohardness and Young's modulus values were extracted from the load–displacement (L–D) dependence using the well-known Oliver–Pharr method [13]. According to the analysis performed by Pelegri and Huang [14], nanohardness measurements are not affected by the unmodified bulk if the indentation depth is smaller than half of the thickness of the modified layer. On the other hand, several studies have proved that the plastic zone developed under the indenter tip can be up to five times that of the indentation depth [15,16]. This effect is less drastic in harder materials with higher yield strength (YS). As reported by Mir et al. [17], heavy ion irradiation of BS3 glasses combined with high indentation load results in development of the plastic zone that is 2–3 times thicker than the plastic penetration depth – confirmed also by Peuget et al. [18]. In conclusion, highly different results show that the only way to correctly identify nanomechanical properties of irradiated layers is to study them under wide indentation loads and dose ranges. In order to investigate the influence of sample roughness, experiments were performed using LPU (Load Partial Unload) method. At each stage, results were repeated at least three times, and the presented curve describes the average value. In order to highlight commonly observed Indentation Size Effect (ISE), hardness of the sample was presented as a function of load and penetration depth, for pristine and irradiated YSZ, see Figs. 1(B) and 2(B), respectively.

3. Results and discussion

Fig. 1(A) presents a load versus displacement plot recorded during LPU – Load Partial Unload test performed in the force range from 1 to 25 mN on pristine YSZ sample. Three visible regions marked as (I), (II) and (III) indicate: sample roughness and ISE – Indentation Size Effect (sources of the measurement error, explained in the following part), estimated maximal indentation depth (implemented during irradiated material testing) and total penetration depth of Ar-ions. As presented in Fig. 1(A), indentation of the pristine YSZ with 1 mN load results in displacement of roughly 50 nm. Due to the similar value of the surface roughness ($R_a \approx 40$ nm) one can expect that the first result will be burden with significant measurement error. This can be verified by calculating the mean hardness values recorded during the LPU test. Thus, if we take into account the whole measuring load range (from 1 to 25 mN), the mean value of hardness is 9.2 ± 1.7 GPa. But, if one omits the initial results (1–3 mN), the reported hardness of the bulk increases to 10 GPa, and the measurement error decreases significantly to 0.3 GPa (region depicted by the black arrow, see Fig. 1A). In order to confirm this statement, hardness vs load and displacement curve is presented in Fig. 1(B). It can be seen that the values of the hardness recorded in the load range 1–3 mN are significantly undervalued in comparison to higher loads. Since the measuring error under load of 1 mN is related to the high roughness of the sample, it can be concluded that the next two low hardness values (measured under 2 and 3 mN loads) could be attributed to the Indentation Size Effect (ISE).

As mentioned in the previous paragraph, Fig. 1(A) presents three regions marked as I, II and III. Region (I) describes the region burdened with the largest measurement error associated with the ISE [19] and roughness of the sample. Reported region should not be taken into account. This will result in a smaller measurement error and more accurate measurement. Region (II) behavior is estimated using the Pelegri et al. [14] rule for maximal indentation depth. The goal of this study was to determine the border of the indentation depth for irradiated sample measurement (no influence of unmodified bulk is expected below this value). Finally, region (III) describes the total penetration depth of Ar^+ ions calculated with the SRIM code [11].

Fig 1(B) presents hardness versus indentation load and displacement. Classical increase of hardness with increasing load (and displacement) can be observed. As explained previously, this phenomenon is very often referred as ISE – Indentation Size Effect [19]. Based on this graph one can identify two regions: (I) region introducing measurement error, and (II) region indicating the most accurate indentation depth for accurate estimation of the mechanical properties of irradiated layers. Based on this analysis, one can conclude that the precise measurement of the implanted layer should be performed in the load range 4–10 mN. This way, we can eliminate the influence of the sample roughness and ISE, and ensure minimal or no impact of the unirradiated bulk material.

According to the literature [2], it is believed that the irradiation leads to creation of radiation defects and residual stresses in the surface layer of the polycrystalline sample. Reported changes should have a significant impact on the nanomechanical properties of the sample. In order to examine the effect of irradiation, polycrystalline samples of YSZ were subjected to Ar-ion implantation with fluences of 10^{14} and 10^{15} $ions/cm^{-2}$.

Fig. 2(A) presents load versus displacement plot recorded during LPU test performed in the force range from 1 to 10 mN on irradiated YSZ. The average values of the hardness and Young's modulus have been given in Fig. 2A) – (calculated in the load range 1–10 mN). One can observe that the build-up of the radiation damage results in hardness increase. Presented results point to the conclusion that at relatively low fluences ion irradiation lead to a slow increase of the stress in the damaged layer. This low stress causes only minor increase of hardness, from 9.2 GPa (pristine YSZ) to 10.4 GPa (1×10^{14} $ions/cm^{-2}$). However, the situation changes when irradiation with a fluence of 10^{15} $ions/cm^{-2}$ takes place. In this case, a significant increase of hardness to almost 15 GPa is observed, see Fig. 2(A). One can state that, at higher fluences, ion irradiation leads to a faster increase of stress in the damaged layer. This may cause destabilization of the structure and defect formation.

Fig. 2(B) presents recorded hardness values versus displacement for irradiated YSZ samples. The numbers from 1 to 10 placed below each of the test points, represent measurement load in mN. It is evident that in each case, hardness values measured under 1–3 mN loads are lower than the given average value. As in the previous case, this is related to the sample roughness and ISE. In con-