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Journal of Nuclear Materials 295 (2001) 121–125

journal of nuclear materials

www.elsevier.nl/locate/jnucmat

Letter to the Editor

Phase transformation of polycrystalline zirconia induced by swift heavy ion irradiation

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Received 13 September 2000; accepted 7 February 2001

Abstract

Polycrystalline samples of monoclinic zirconia (α-ZrO_2) have been irradiated at room temperature with 190 MeV ^{36}Ar and 170 MeV ^{84}Kr ions in the electronic slowing down regime. Room-temperature X-ray diffraction (XRD) and micro-Raman spectroscopy measurements show consistently that a phase transition to the tetragonal form (β-ZrO_2) occurs for 170 MeV ^{84}Kr ion irradiation above an electronic stopping power value around 15 MeV μm^{-1}. The kinetics of the transition were monitored by on-line XRD measurements on the same sample. No such phase transformation is seen with 190 MeV ^{36}Ar ion irradiation for an electronic stopping power value around 6 MeV μm^{-1}. The plot of the tetragonal phase fraction deduced from XRD measurements vs fluence is analysed with single-impact and double-impact kinetic models. The data seem to be in favour of a double ion impact process.

1. Introduction

Since the end of the 1950s, a number of studies has been done on the effects of different kinds of radiation on zirconium dioxide (ZrO_2) or zirconia. In standard temperature and pressure conditions, the thermodynamically stable phase of zirconia is the monoclinic one (α-ZrO_2) with a structure belonging to the $P2_1/c$ space group. At increasing temperature, zirconia first transforms to a tetragonal form (β-ZrO_2) between 1000°C and 1200°C, and then to a cubic form (γ-ZrO_2) at about 2300°C. The β and γ phases belong respectively to the $P4_2/nmc$ and Fm3m space groups.

Wittels and Sherrill [1,2] concluded that the monoclinic (α) to cubic (γ) or tetragonal (β) phase transformation of ZrO_2 under fast neutron irradiations could be induced by a 'fission-spike' mechanism. However, further studies contradicted these first data by claiming that impurities are needed to aid the inhomogeneous nucleation of the cubic phase [3,4]. Recent results also show that this transformation does occur under 340 keV Xe ion irradiation at 120 K [5] and 800 keV Bi ion irradiation at 300 K [6] in the nuclear slowing down regime.

Moreover, it is also known that structural changes can occur in some materials under a high density of electronic excitations. In the case of a metal like titanium, it was shown that a displacive or martensitic-type transition from the α to the ω phases can be triggered by the dense electronic excitations generated in the wake of swift heavy ions [7]. A change from a cubic to a monoclinic phase was also found in an insulator like Y_2O_3 with swift heavy ion irradiations above an electronic stopping power threshold near 10 MeV μm^{-1} [8], that was interpreted by a pressure effect due to the thermal spike generated in the ion wake [9]. The likelihood of a similar process in the case of zirconia is addressed here: we bring clear experimental evidence that the $\alpha \rightarrow \beta$ phase transition does occur in monoclinic

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0022-3115/01/$ - see front matter
PII: S0022-3115(01)00506-2

Table 1
Typical analysis of the zirconia powder used in this work

Compounds	$ZrO_2 + HfO_2$	SiO_2	Fe_2O_3	TiO_2	Na_2O	Al_2O_3	SO_4	Cl
Wt%	99.6	0.02	0.002	0.11	0.01	0.03	0.05	0.03

zirconia as a result of an heavy ion irradiation in the electronic slowing down regime [10].

2. Experimental procedure

We used a powder supplied by Goodfellow made of monoclinic zirconia (α-ZrO_2) with a small amount of tetragonal zirconia (β-ZrO_2) (<5%) and a mean grain size about 1 μm. The typical chemical analysis of the powder is given in Table 1. This powder was pressed (1 metric ton cm^{-2}) at room temperature and submitted to a thermal treatment (950°C – 12 h) in order to suppress the residual β-ZrO_2 and improve the mechanical behaviour. The X-ray powder diffraction (XRD) spectra of pristine pellets before irradiation were performed on a D 500 SIEMENS equipment using the Cu-Kα radiation, in the Bragg–Brentano configuration [10].

Samples have been exposed under normal incidence to 190 MeV ^{36}Ar and 170 MeV ^{84}Kr ions in the electronic slowing down regime (Table 2) at room temperature and under high vacuum. The electronic (S_e) and nuclear (S_n) energy losses were calculated with the SRIM2000-38/TRIM code [12]. The ion flux was less than 5×10^8 cm^{-2} s^{-1} in order to avoid charging and temperature effects at the most. These irradiations were carried out on the medium energy line (SME) at GANIL in Caen, France. On-line XRD measurements were performed in the CHEXPIR set-up with Cu-Kα radiation and an INEL curved detector at a fixed incidence angle so that the analysed depth (about 4.5 μm) was clearly lower than the ion projected ranges (Table 2). A calibration was done with a silicon standard. The acquisition time was, in most cases, limited to 30 min in order to optimise the ion beam time. Irradiations had to be stopped during the XRD measurements so as to reduce the γ-ray activation signal background. Off-line micro-Raman microscopy was used to characterise the samples with a T-64000 confocal Jobin–Yvon spectrometer using the 514 nm spectrum line of an argon laser with beam spot of 1 μm^2. A laser output smaller than 300 mW was used to avoid sample damage [10]. The analysed depth in zirconia with an absorption coefficient of 0.4 μm^{-1} is a few micrometres [11].

Table 2
Characteristics of the irradiations of monoclinic zirconia (α-ZrO_2) with a mass density of 5.82 g cm^{-3} [a]

Ion	^{36}Ar	^{84}Kr
E (MeV)	190	170
ϕt_{max} (cm^{-2})	1.0×10^{14}	1.05×10^{14}
R_p (μm)	27	13
S_n (keV μm^{-1})	5	37
S_e (MeV μm^{-1})	6.1–6.6	15.6–18.3

[a] E – total energy of ions, ϕt_{max} – maximum fluence, R_p – mean projected range), S_e – minimum and maximum values of the electronic energy loss for a depth less than 6 μm), S_n – nuclear energy loss at the pellet surface) computed with the SRIM2000 code [12].

3. Results

The XRD pattern of the mineralogical compound named baddeleyite is well known and fits the unirradiated pellet pattern with a small amount of tetragonal phase (<5%) [10]. After annealing at 950°C, the latter phase is seen to disappear (Fig. 1(a)). For the 170 MeV

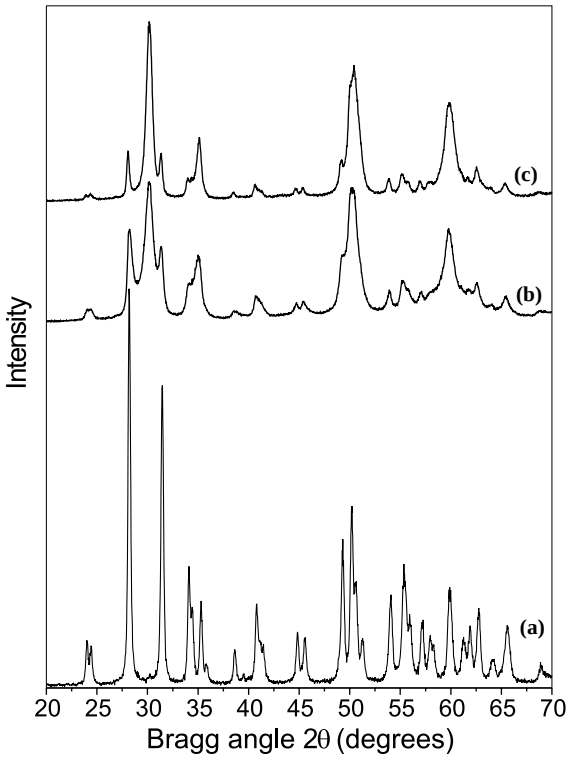

Fig. 1. XRD patterns of the pristine monoclinic zirconia (α-ZrO_2) powder after heat treatment at 950°C – 12 h (a), and after irradiation with 170 MeV ^{84}Kr ions at a fluence of 1.31×10^{13} cm^{-2} (b), and 1.05×10^{14} cm^{-2} (c).

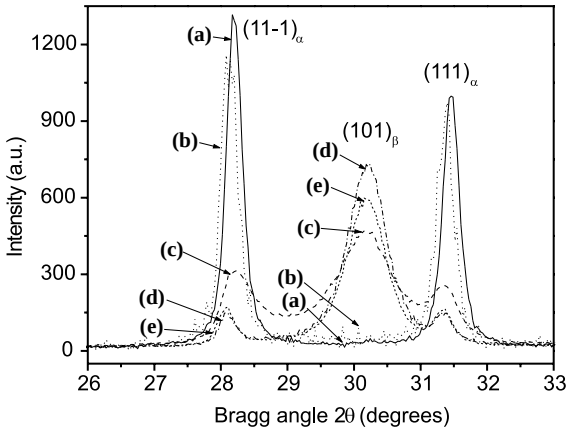

Fig. 2. XRD patterns of monoclinic zirconia (α-ZrO_2) (a) irradiated with 170 MeV ^{84}Kr ions displayed over a small 2θ range near 30° in order to follow the α-$ZrO_2 \rightarrow$ β-ZrO_2 (tetragonal) transformation vs ion fluence: 1.08×10^{12} cm^{-2} (b), 1.31×10^{13} cm^{-2} (c), 4×10^{13} cm^{-2} (d), and 1.05×10^{14} cm^{-2} (e).

^{84}Kr ion irradiations, the on-line XRD patterns clearly show the appearance of new peaks while those of the monoclinic phase decrease (Figs. 1 and 2). The new peaks belong to an allotropic phase of zirconia, but because of peak overlaps, it was not possible to accurately identify its crystal structure. No such changes occur in the case of the 190 MeV ^{36}Ar ion irradiations up to the maximum fluence of 1×10^{14} cm^{-2} (Fig. 3).

In order to clear up this point, off-line Raman spectra have been obtained on the two pellets irradiated, respectively, with 170 MeV ^{84}Kr (Fig. 4) and 190 MeV ^{36}Ar ions (not shown) at the maximum fluence of 1×10^{14} cm^{-2}. The experimental Raman bands of the pristine (Fig. 4(a)) and Kr-irradiated (Fig. 4(b)) samples are compared with those of α-ZrO_2 and β-ZrO_2. A good agreement is found between the wave numbers of the pristine sample and the calculated [6] and experimental [13] values of the monoclinic phase (Fig. 4(a)), and of the new peaks appearing in Fig. 4(b) with those of the tetragonal phase [6,13] (see Table 3). Note that the peaks at 77 and 116 cm^{-1} in Fig. 4 correspond to plasma laser lines. Raman analysis of the Kr-irradiated sample thus shows that the new phase is the tetragonal one, and confirms that the α-$ZrO_2 \rightarrow$ β-ZrO_2 transformation is almost complete, whereas no transition is detected with the 190 MeV ^{36}Ar ion irradiation.

Although the total XRD intensity is decreasing with irradiation dose, the XRD background does not display any evidence of an amorphous phase. Therefore our quantitative phase calculation will only take into account α-ZrO_2 and β-ZrO_2. Among all the existing formulae used for the β phase percentage calculation (X_β) in an allotropic mixture of zirconia, we chose that of

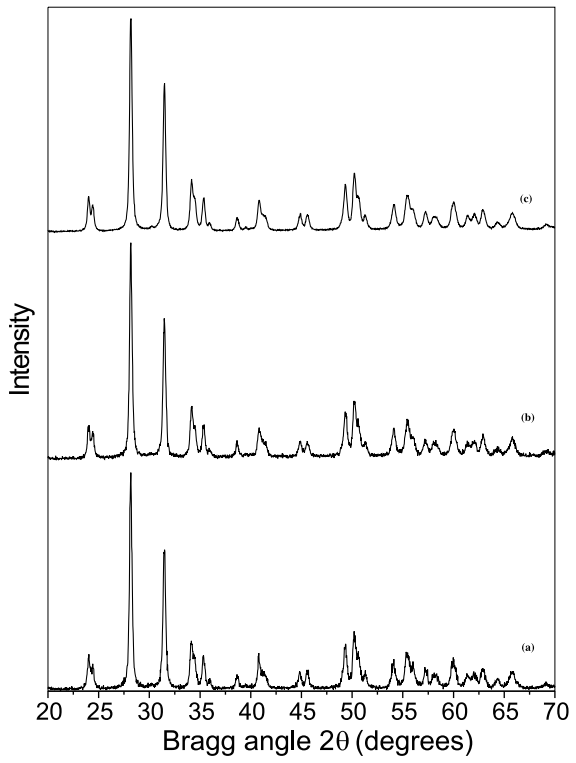

Fig. 3. XRD patterns of the pristine monoclinic zirconia (α-ZrO_2) powder after heat treatment at 950°C – 12 h (a), and after irradiation with 190 MeV ^{36}Ar ions at a fluence of 1.92×10^{13} cm^{-2} (b), and 1×10^{14} cm^{-2} (c).

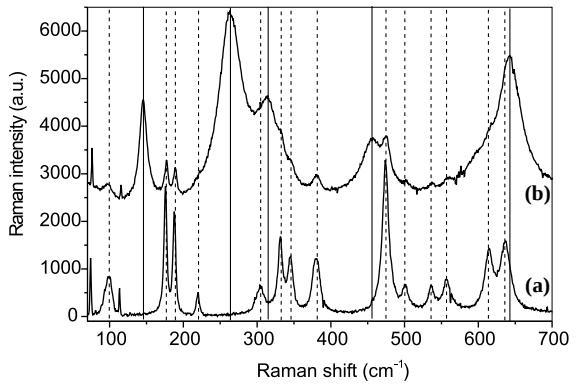

Fig. 4. Raman spectrum of the monoclinic zirconia (α-ZrO_2) pellet before (a) and after irradiation with 170 MeV ^{84}Kr ions at a fluence of 1.05×10^{14} cm^{-2} (b): the major Raman peaks of α-ZrO_2 (monoclinic) and β-ZrO_2 (tetragonal) are respectively marked by the dashed and solid lines (see Table 3).

Garvie and Nicholson [14] taking into account the (1 0 1) reflection of the β phase which is not overlapped by the α phase reflections:

Table 3
Calculated [6] and experimental values [13] of the Raman frequencies of α-ZrO_2 and β-ZrO_2 (yttrium-doped zirconia) compared to the present data of the monoclinic zirconia (α-ZrO_2) sample irradiated with 170 MeV Kr ions at a fluence of 1.05×10^{14} cm^{-2} with 90% volume fraction of the tetragonal phase (β-ZrO_2)

Monoclinic			Tetragonal		
Calculation [6] (cm^{-1})	This work (cm^{-1})	Experimental [13] (cm^{-1})	Calculation [6] (cm^{-1})	This work (cm^{-1})	Experimental [13] (cm^{-1})
631		625	645	643	630
606		605	577		595
570	557	554	471		465
521	541	534	456	454	410
505		500	?	314	305
477	474	476	260	261	257
382	380	392	188	146	155
344		334			
327		323			
309		297			
242		221			
204	189	193			
184	177	183			
128	99	115			

$$X_\beta = \frac{I(101)_\beta}{I(11\bar{1})_\alpha + I(101)_\beta + I(111)_\alpha}, \quad (1)$$

where $I(hkl)_i$ is the area of the peak (hkl) of the phase i which is measured by using the Siemens profile decomposition software with Pseudo-Voigt curves [10]. This formula has been satisfactory tested in our laboratory for known powders with a variable tetragonal to monoclinic phase volume ratio [10]. Fig. 5 displays the plot of the β-ZrO_2 volume fraction vs fluence for the 170 MeV ^{84}Kr ion irradiation which exhibits a saturation at around 90% of β-ZrO_2 above a fluence about 2×10^{13} cm^{-2}.

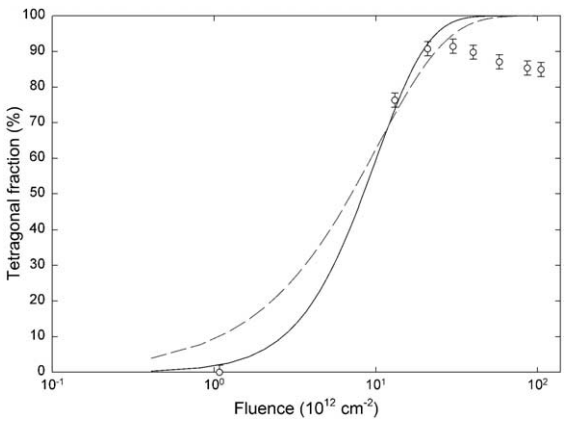

Fig. 5. Fraction (X_β) of tetragonal zirconia (β-ZrO_2) vs ion fluence for the 170 MeV ^{84}Kr ion irradiations (open circles) with the best least-squares fits using the single-impact (dashed) and double-impact (solid) models.

4. Discussion

The present XRD data give a clear evidence that a phase transformation occurs in monoclinic zirconia under a swift heavy ion irradiation in the electronic slowing down regime, above a threshold value of S_e comprised between 6.5 and 15 MeV μm^{-1}. Moreover, the Raman data show that the resulting phase is the tetragonal one, in agreement with the data obtained with 800 keV Bi ion irradiations in the nuclear slowing down regime [6].

In general, swift heavy ion irradiations are known to produce metastable crystalline or amorphous forms due to the out-of-equilibrium process. In the present case, the evidence of the tetragonal phase was obtained by the XRD data just after the beam was shut off, and also by the Raman data two months later, showing that this phase was stable at room temperature. This can be explained by the quenched-in defects in the process and/or to related irradiation-induced stresses stabilizing the tetragonal phase at room temperature.

The $\alpha \rightarrow \beta$ transition is almost complete (85–90%) at a fluence around 2×10^{13} cm^{-2} which indicates that this process is compatible with a track effect with a cross-section around 10^{-13} cm^2 corresponding to a track radius around 2 nm. However, the data of the tetragonal phase fraction (X_β) vs fluence (ϕt) (Fig. 5) do not seem to be compatible with a simple single-impact process according to the classical Poisson's law such as

$$X_\beta = 1 - \exp(-A\phi t) \quad (2)$$

with a single cross-section $A = 9.8 \times 10^{-14}$ cm^2, because at $\phi t = 1.1 \times 10^{12}$ cm^{-2} the tetragonal phase content is

smaller than the detection limit of the technique i.e., 1%. With a simple single-impact process, Eq. (2) gives $X_\beta = 10.2\%$. It suggests that other kinetic models like the double-overlap ones would be more relevant since these models imply that the first derivative of X_β vs ϕt at zero fluence would be zero. It seems to be the case here, while the single-impact one exhibits a linear increase vs ϕt at low fluence.

We have thus checked a double-impact kinetic model to fit these data, and try to deduce a damage cross-section. In this framework, it is assumed that when at least two impacts occur within a section σ around a given point of the target, the whole section σ undergoes a phase transformation. This process yields the following equation:

$$X_\beta = 1 - (1 + \sigma\phi t)\exp(-\sigma\phi t). \quad (3)$$

Such a kinetic process does give a zero first derivative of X_β vs ϕt at $\phi t = 0$. The cross-section deduced from the best non-linear least-squares fit is $\sigma = 2.0 \pm 0.3 \times 10^{-13}$ cm^2 with the corresponding fitted curve plotted in Fig. 5, which seems in good agreement with the shape of the experimental curve. However, two problems arise with the present results, namely that (i) we never observe a complete transformation to the β phase (at maximum 90%) and (ii) low-fluence data are lacking. It is to be noted that in the case of the transition induced by nuclear collisions, a similar sigmoid curve vs fluence with a saturation at around 80% is also observed [6]. This incomplete transformation could be due to some physical reason linked to the transformation mechanism. More experimental data are needed in order to conclude more precisely on this point.

New data at intermediate S_e values have confirmed the sigmoid curve shape corresponding to a double-impact process with a saturation at around 80% [15]. Moreover, it must be checked if a single-impact kinetics could occur at much larger S_e values. Since β-ZrO_2 is a high-pressure and high-temperature phase, the out-of-equilibrium process stabilising the tetragonal phase at room temperature must be addressed. It might involve a thermal and/or a pressure effect due to the thermal spike generated in the ion tracks like in Y_2O_3 [9].

5. Conclusions

By using XRD and Raman spectroscopy, we have shown that a crystalline phase transition occurs in monoclinic zirconia (α-ZrO_2) to the tetragonal phase (β-ZrO_2) under 170 MeV ^{84}Kr ion irradiation in the electronic slowing down regime, above an electronic stopping power value around 15 MeV μm^{-1}, whereas it does not occur with 190 MeV ^{36}Ar ion irradiation at around 6 MeV μm^{-1}. However, the transformation is not complete and levels off at around 90%. The plot of the tetragonal phase fraction deduced from the XRD data vs fluence does not seem to be compatible with a single-impact kinetic model. The data are thus analysed with a double-track overlap model using a single track cross-section which yields a cross-section around 2×10^{-13} cm^2. However, these results are going to be further refined and confirmed with swift heavy ion irradiations at electronic stopping power values ranging between 6 and 15 MeV μm^{-1} in order to determine the transition threshold more precisely and check the kinetics of the transition.

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