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Stress analysis of zirconia studied by Raman spectroscopy at low temperatures ☆

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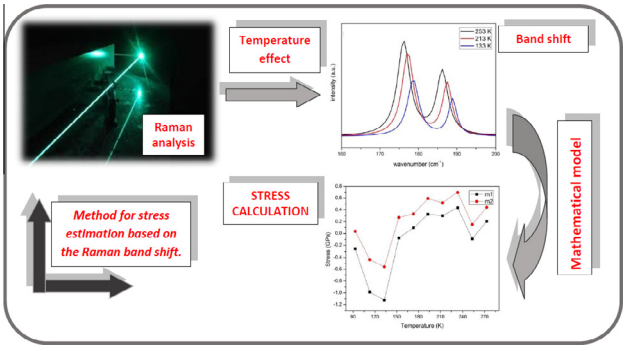
HIGHLIGHTS

- Raman bands of monoclinic phase have been studied upon decreasing temperature.
- Method of stress calculation is proposed.
- Decreasing temperature increases level of compressive stress.
- Pre oxidation temperature has a significant impact on the stress level in the oxide.

GRAPHICAL ABSTRACT



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ABSTRACT

The paper presents effect of low temperature upon location of selected Raman bands. The structural properties of pure zirconium pre-oxidized at 773 K and 873 K have been studied during cooling in the range of temperatures 273 K and 93 K by Raman spectroscopy. Analysis of the Raman band positions for the monoclinic phase of zirconia oxide was performed. Raman spectroscopy has shown that monoclinic phase of zirconia oxide undergoes a continuous band displacement, individual for each studied Raman mode. Registered shift is aimed towards the high frequency direction. Recorded Raman band displacement was employed to study stress state in zirconia oxide films grown on pure zirconium developed during control cooling. Presented results showed a good correlation between different thicknesses of the oxide scale.

Introduction

Raman spectroscopy is a powerful tool to investigate structural changes of zirconia samples subjected to the external influences [1]. Therefore, among numerous analytical methods this one has been chosen to investigate the properties of zirconia scale. It is well known, that the oxide layer, which develops during zirconium corrosion, results in a mixture of tetragonal and monoclinic polymorphs. Generally, the tetragonal layer is preferentially located in the proximity of the metal/oxide interface, and the oxide film can be divided into two sub-layers: reach in tetragonal and reach in monoclinic oxide phases [2–4]. Although the literature is reach in studies performed at elevated temperatures [5–8],

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understanding mechanisms operating in low temperatures is still poorly presented [9].

Reported contribution deals with the problem of zirconia subjected to effect of low temperatures and stress state arising in the oxide layer. In order to create a sufficient layer of oxide, studied sample was pre-oxidized at 773 K and 873 K for 7 h. The idea of this experiment was to investigate a negative volume variation caused by temperature decrease, estimate the stress state and check whether the structural evolution is susceptible to the same extent as in the case of negative volume variation induced by pressure. As presented by Bouvier [10] most of the Raman modes exhibit positive shift (higher frequency direction) with the exception of the purely tetragonal phase mode located at 260 cm^{-1} which decreases when pressure increases. This phenomenon is in full concord with presented studies.

Materials and methods

Material and conditions of oxidation

The material chosen for this study (pure zirconium plate, purity 99.8%) was provided as a 0.5 (mm) thick sheet processed by Good-Fellow Cambridge Ltd., and its detailed composition is given in Table 1. From the sheet, sets of samples were cut in order to perform isothermal oxidation: $2 \times 2 \times 0.5$ mm pieces for Raman measurements. All samples were heated at 873 K for 1 h in order to eliminate internal stress created during the industrial preparation. After that, the samples were mechanically polished with paper up to grade 1000×, cleaned with ethanol and dried.

As reported by several authors, oxidation kinetics of zirconium occurs in two stages [3,5–7]. In the first stage, a thin layer of oxide is created and the oxidation process proceeds according to the parabolic law. In the second stage, the process is greatly accelerated and proceeds according to the linear law [7]. In order to obtain accurate results, a thick oxide layer is necessary. This can be achieved by choosing sufficiently high oxidation temperatures. Therefore, pre-oxidation was performed using air during 7 h, under normal pressure at two various temperatures: 773 K and 873 K. In conclusion, reported conditions were chosen as a compromise between oxidation time and achieving sufficient oxide layer thickness in order to conduct valuable Raman analysis. In order to avoid producing excessive thermal stresses arising from the different thermal expansion coefficients of oxide and metal, the controlled cooling process to room temperature with speed of 373 K/h was employed.

Low temperature Raman spectroscopy

Oxide scale developed on zirconium during high temperature oxidation consists of two polymorphs: monoclinic and tetragonal phases [11–13]. Tetragonal phase is located in the vicinity of the metal and the external part of the scale consists mostly in monoclinic phase. Presented contribution is based on the Raman spectroscopy technique, which allows collecting information from about 1 μm depth in the conditions used in the present study. From the thermo-gravimetric measurements, it appears that the oxide scale has a thickness of about 1.5 and 4 μm after oxidation at 773 K and 873 K respectively [4]. This may cause distortion of the tetragonal phase signal. Moreover, several authors [14,15] reported that many bands of zirconia phases are highly sensitive to the effect of temperature and increasing stress in the oxide. Based on these considerations, two bands characteristic for the monoclinic phase has been selected as a reference for further stress calculations. These two bands have been selected due to the strong signal and low distortion arising from the presence of near-located bands of the tetragonal phase, as reported by Barberis [16]. To make the reading of the next sections easier, chosen analytical wavenumbers relating to monoclinic phase, located at room temperature at 177 and 188 cm^{-1} will be abbreviated as "m1" and "m2" bands. These are the band positions chosen for the stress calculations.

The Raman spectra have been recorded using the three-gratings micro-Raman spectrometer T-64000 (Jobin–Yvon) equipped with confocal microscope (Olympus). A long working distance objective ×50 (N.A. = 0.5) was selected what allowed to obtain a laser spot with diameter of about 2.5 μm. All measurements were performed in a backscattering micro-configuration using the 514.5 nm line from an Ar-ion laser. The power of the laser light on the surface of the sample was 3 mW. The low temperature measurements were conducted in He/N_2 cryostat with accuracy of ±1 K. Before the Raman spectrum acquisition, the sample was stabilized at given temperature at least 3 min. The heating/cooling rate was 2 K/min. To obtain the high quality signal/noise ratio, the four measurement cycles were averaged before the statistical treatment.

Positions of the selected bands m1 and m2, have been calculated assuming the lorentzian shape of all bands (PeakFit v4.12 software was used for data analysis). Therefore, the corresponding wavenumbers v are given as a function of the temperature. In order to calibrate this methodology, a stress free sample is needed to obtain the stress free state. To deduce the stress free wavenumber, evolution of m1 and m2 bands with temperature is necessary. This has been done based on the work of Bouvier [10] where a zirconia powder has been heated from room temperature to 973 K. The corresponding wavenumber v is thus obtained for the oxidation temperature, which allows taking into account the thermal effect on the Raman band position. Afterwards, due to the lack of reliable data performed in low temperatures and linear Raman band shift at high temperature an extrapolation of Raman bands has been performed. Reported wavenumbers were thus obtained and the stress free reference spectrum for each low temperature measurement has been deduced. As reported in [17], the monoclinic phase in the oxide can adequately represent the "stress free state" of the oxide scale, so can serve as a suitable standard.

Evolutions of the m1 and m2 bands recorded during temperature decrease are shown in Figs. 1 and 2 for the sample oxidized at 773 K and 873 K respectively. Then, the stress determination in the oxide scale becomes possible based on the variation of the wavenumber with respect to the reference position at working temperature. Variation of Δv for m1 and m2 modes has been used to deduce the corresponding stress σ_{ox} according to the following equations:

$$\Delta v = v(T,\sigma) - v(T,0) \tag{1}$$

$$\text{Peak at } 177\ cm^{-1}\ \sigma_{ox} = -0.683\Delta v \pm 0.02 \tag{2}$$

$$\text{Peak at } 188\ cm^{-1}\ \sigma_{ox} = -0.528\Delta v \pm 0.04 \tag{3}$$

Table 1
Composition of the studied material.

Element	C (ppm)	Hf (ppm)	Fe (ppm)	Cr (ppm)	N (ppm)	O_2 (ppm)	H (ppm)
Zr purity 99.8 + %	250	2500	200	200	100	1000	10