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The use of Larson–Miller parameters to monitor the evolution of Raman lines of tetragonal zirconia with high temperature aging

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Abstract

The evolution of the Raman lines of metastable tetragonal yttria-stabilized zirconia with annealing for different times at different high temperatures has been monitored and the data analyzed using a Larson–Miller parameter. This normalization allowed the shift and sharpening of the Raman peaks of tetragonal zirconias having different stabilizer concentration and produced by different methods with different microstructures to be described by a common curve. The observed Raman shifts are consistent with evolution into a coherent mixture of tetragonal and cubic phases.

Keywords: Raman spectroscopy; Zirconia; High temperature aging

1. Introduction

In their studies of the effect of stress and temperature on the creep rupture time of gas turbine alloys, Larson and Miller showed that their results could be collapsed onto a common curve using a normalization of the form $LMP = T[C + \ln(t)]$ [1]. This normalization has been widely used since as a phenomenological method to relate the effects of time and temperature on various thermally activated processes. In this work we show that the Larson–Miller normalization can be employed to monitor changes in the Raman lines from yttria-stabilized zirconia as phase evolution occurs at high temperatures, in some instances before phase evolution is apparent by X-ray diffraction. This has important consequences for non-contact phase transformation studies as well as for condition assessment of zirconia-based coatings in high-temperature applications.

Tetragonal zirconia can only exist as a stable phase over a narrow range of high temperatures and yttria concentration (Fig. 1). The tetragonal phase is generally metastable with respect to their monoclinic and cubic polymorphs. Furthermore, while oxygen diffusion is very fast in yttria-stabilized zirconia – and is the basis for solid oxide fuel cells and oxygen sensors – cation diffusion is very slow. Consequently, equilibration of the tetragonal phase can take very long times, even at temperatures above 1000 °C [2]. These considerations are especially important for applications, such as thermal barrier coatings, which rely on the long-term, high-temperature stability of yttria-stabilized zirconia as well as its very low thermal conductivity. The optimum compositions for thermal barrier coatings have been found to be those shown in the grey box in Fig. 1 [3]. On prolonged high temperature exposure, these compositions, which are denoted tetragonal-prime, evolve into a mixture of the equilibrium cubic (yttrium-rich) and tetragonal (yttrium-poor) phases.

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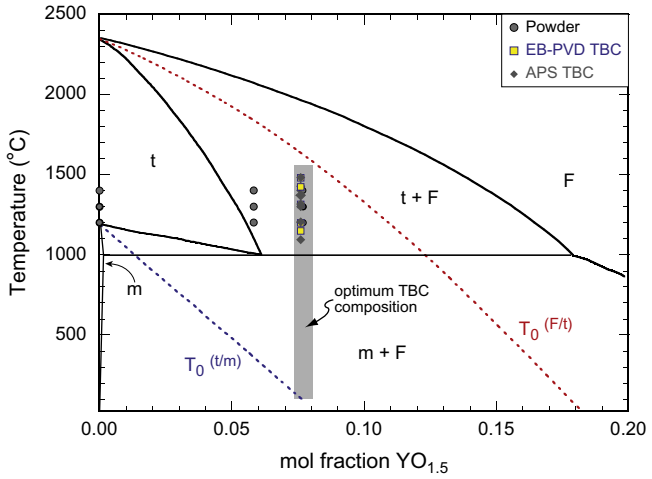

Fig. 1. Zirconia-rich portion of the ZrO_2–$YO_{1.5}$ phase diagram, showing the concentrations and aging temperatures used in this study. Both the equilibrium and metastable boundaries of the monoclinic, tetragonal and cubic phase fields are shown.

As part of a collaborative program investigating the phase evolution of tetragonal zirconia in thermal barrier coatings prepared by air plasma spraying (APS) and electron beam physical vapor deposition (EB–PVD), we have noticed that even before the onset of transformation to any monoclinic phase, the Raman peaks of tetragonal zirconia change with annealing at high temperatures. These observations, made on a series of zirconia powders and coatings after annealing for different times at different temperatures, are described in this work. We show that the changes in the peak position and peak width can be normalized using the Larson–Miller relation. Furthermore, the observed changes suggest that coherency strains arise during the initial stages of phase evolution.

2. Experimental details

2.1. Powders and coatings

Commercially available monoclinic and tetragonal zirconia powders with different concentrations of yttria (Table 1) were purchased from Tosoh Corp. (Tokyo, Japan). A variety of 7YSZ coatings (7 wt.% Y_2O_3 – stabilized ZrO_2) made by air plasma spraying (APS) and electron beam–physical vapor deposition (EB–PVD) were obtained from several sources, also listed in Table 1. The powders and coatings were annealed for different times and at different temperatures in air, as indicated Fig. 1. The heating and cooling rates varied from 10 °C min^{-1} (for heat treatment in a standard furnace) up to 300 °C min^{-1} (for annealing in a thermal cycling rig). As the Raman spectra from the as-received, nominally tetragonal Tosoh powders indicated that they were partially transformed to monoclinic, they were first all annealed at 1200 °C for 5 h. After this pre-treatment, all the powders except for the pure zirconia (0YS) were single-phase tetragonal.

Table 1
Composition of yttria-stabilized zirconia materials examined in this study.

Specimen	Designation[a]	mol.% $YO_{1.5}$	Phase
Powder	0YS	0	Monoclinic
Powder	3YS	5.8	Tetragonal
Powder	4YS	7.7	Tetragonal
APS	7YSZ	7.6	Tetragonal
EB–PVD	7YSZ	7.6	Tetragonal

[a] Designation of powder from Tosoh corresponds to the mol.% of Y_2O_3 in ZrO_2 while the convention used in thermal barrier coating applications is to refer to the concentration in wt.% of Y_2O_3 in ZrO_2.

2.2. Raman measurement and spectral analysis

Raman spectra were obtained from the coatings and powders using a LabRAM Aramis Raman system (Horiba Jobin Yvon, Edison, NJ) using the 633 nm excitation of a He–Ne laser operated at room temperature. The Raman spectra were acquired on a relatively large area, using a 10 μm diameter laser beam. Because of the translucency of zirconia and the sampling depth of collection optics, the spectra were obtained from a sufficiently large volume to encompass the statistical variations. The spectra recorded were subsequently deconvoluted using commercial peak-fitting software (GRAMS, Thermo Electron Corp., Philadelphia, PA) assuming mixed Lorentzian and Gaussian profiles for the Raman lines at 465, 610 and 640 cm^{-1}. The characteristic Raman lines of tetragonal zirconia at 145, 260 and 320 cm^{-1} are asymmetric and hence were fitted using a Breit–Wigner profile (an asymmetric Lorentzian function) [4] using the OriginPro package (OriginLab Corp., Northampton, MA). The peak positions were calibrated by also monitoring the laser Rayleigh line at 0 cm^{-1}.

3. Results

The Raman spectra of the monoclinic and tetragonal zirconia were consistent with prior reports and examples are shown in Fig. 2 as a function of annealing time and temperature. The positions and widths of the monoclinic peaks did not show any systematic change with either duration or temperature of annealing, as illustrated in Fig. 3. (The peak at around 103 cm^{-1} was selected because it has the most pronounced changes with aging compared to the other monoclinic peaks.)

By contrast, the tetragonal peaks shifted and narrowed with annealing time and temperature as illustrated by Fig. 4. For analysis, we selected three Raman peaks characteristic of the tetragonal phase, namely 145 cm^{-1} (E_g mode), 260 cm^{-1} (A_{1g} mode) and 465 cm^{-1} (E_g) because they have good intensities and are well isolated from other peaks, thereby minimizing errors associated with peak fitting and background subtraction. The mode assignment adopted in this work follow those proposed by Milman et al. [5] although other, older assignments have been pro-