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Low-temperature transformation kinetics of electron-beam deposited 5 wt.% yttria-stabilized zirconia

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Abstract

The transformation kinetics of ZrO_2 coatings stabilized with 5.6 mol% $YO_{1.5}$ (5YSZ), and deposited by electron-beam physical vapor deposition, were studied between room temperature and 600 °C using in situ Raman spectroscopy, and are described in the form of a transformation-time–temperature diagram. The coatings were found to be monoclinic (m) at temperatures below 375 °C, while above 400 °C they transformed to the tetragonal (t) phase. On cooling, the coatings transformed back to monoclinic below ∼375 °C. Between 375 and 400 °C, the transformation rates approached zero, indicating that the thermodynamic driving force for the transformation also approaches zero in this temperature range. This provides a direct measurement of the T_0(m–t) temperature for the 5YSZ composition.

Keywords: Thermally activated processes; Phase transformation kinetics; Raman spectroscopy; Yttria-stabilized zirconia

1. Introduction

The tetragonal (t)–monoclinic (m) phase transformation in zirconia remains one of the most intensively studied of all transformations in oxides. The basic crystallography [1], its martensitic character [2] and the approximate phase boundaries [3] as a function of stabilizer concentration were all identified well before it was recognized that it could be exploited in transformation toughening of ceramics [4]. In the heyday of transformation toughening, numerous studies were carried out detailing the transformation in various zirconia base compositions, including a variety of studies demonstrating that the transformation could be triggered in a zone about a propagating crack [5,6]. Although many of the envisaged applications of transformation toughening have not been realized commercially, the material was used for several years in hip implants. In these prosthetic devices, the material is formed by conventional ceramic routes with a typical composition of about 6 mol% $YO_{1.5}$–ZrO_2 and the material is tetragonal. Gradually, however, problems developed with some of the zirconia implants in the body [7]. These were identified as being due to a low-temperature degradation phenomenon in which the ceramics slowly transformed from their as-fabricated tetragonal phase to the monoclinic phase with consequent decrease in strength. Although the mechanism of the transformation remains elusive, there is a consensus that it occurs in the presence of moisture at temperatures between room temperature and 200–400 °C.

One of the other major applications of yttria-stabilized zirconia is as a thermal barrier coating. In this application, the material is deposited as a thick coating (∼100–3000 μm) onto metallic components in order to provide a measure of thermal protection. These coatings, whether deposited by plasma-spraying or electron-beam evaporation, are in a metastable state that is commonly referred to as tetragonal-prime. The maximum cyclic life of coatings occurs when the coatings have a composition of about 8 wt.% $YO_{1.5}$–ZrO_2, known as 8YSZ and corresponding to 8.6 mol% $YO_{1.5}$–ZrO_2. At high temperatures, the metasta-

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ble tetragonal-prime phase slowly partitions into a mixture of an yttria-rich cubic phase ($\sim$17 mol% $YO_{1.5}$) and an yttria-poor tetragonal phase ($\sim$4 mol% $YO_{1.5}$), in accord with the equilibrium phase diagram [8]. The majority of studies of TBC coatings have indicated that the metastable structure does not transform on cooling but recently we have found that electron-beam physical vapor deposition (EB-PVD) coatings subject to prolonged annealing at 1425 °C, a higher temperature than coatings are exposed to in gas turbine engines, will very slowly transform to monoclinic at low temperatures [9]. It seems therefore that the metastable zirconia formed by EB-PVD is also susceptible to the same low-temperature degradation phenomenon as ceramic forms.

Recent thermodynamic calculations have predicted the position of the T_0 lines for the t–m transformation and the tetragonal–cubic transformations as a function of the concentration of the yttria-stabilizer [10]. According to metastable equilibria considerations, tetragonal zirconia cooled below the T_0(t–m) line will transform to the monoclinic form and will transform back on heating above the T_0 line. Inspection of the computed phase diagram in Fig. 1 shows that 5YSZ crosses the calculated T_0(t–m) line at a temperature of about 425 °C, meaning that above that temperature the metastable equilibrium will lead to the formation of tetragonal zirconia, whereas below the equilibrium monoclinic phase is preferred. To our knowledge, no systematic study has been performed to validate the position of the metastable t–m boundary. Part of the scope of the experiments described here is to determine the boundary for the 5YSZ composition. The other is to determine the kinetics of the transformation. In this study we use in situ Raman spectroscopy to monitor the kinetics of both the t → m and the m → t transformation, between room temperature and 600 °C, in thick 5YSZ coatings deposited by EB-PVD.

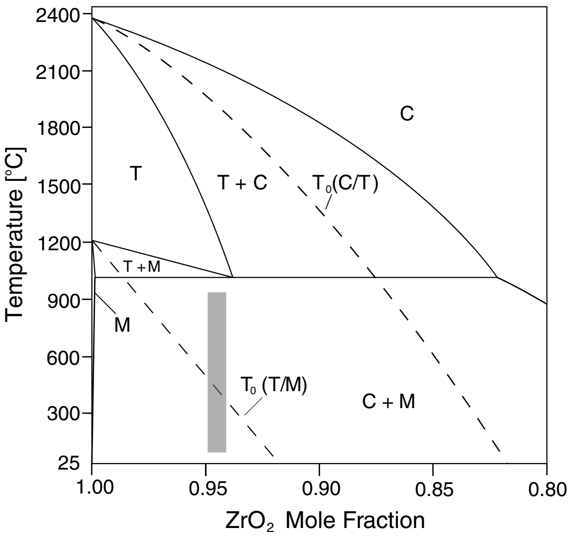

Fig. 1. Phase diagram of the system ZrO_2–$YO_{1.5}$ (redrawn from Ref. [10]). The highlighted area represents the range of compositions around 5.6 mol% $YO_{1.5}$ (5YSZ) and the range of temperatures of interest of this study. In the region above the T_0(t–m) line the tetragonal phase is favored, whereas below the line the system tends toward the equilibrium monoclinic phase.

2. Experimental details

All the experiments described here were carried out in laboratory air (average humidity $\sim$60%) on a coating deposited by electron-beam evaporation at an approximate temperature of 1000 °C onto a 1 in. diameter superalloy coupon. The nominal composition was 4 wt.% Y_2O_3–ZrO_2, i.e. 4.4 mol% $YO_{1.5}$–ZrO_2. However, X-ray diffraction measurement of the lattice parameter ratio (c/a ratio) in its tetragonal form (Fig. 2a) indicated, by applying the empirical formula proposed by Miller et al. [11], a composition of 5.6 mol% $YO_{1.5}$, corresponding to 5 wt.% Y_2O_3–ZrO_2, i.e. 5YSZ. This is the composition we shall refer to hereafter. The material had a thickness of approximately 140 µm, and a columnar microstructure, illustrated in Fig. 2b, typical of electron-beam deposition [12]. A small (approximately 1 mm × 1 mm × 3 mm) portion of the material was cut in order to fit into the crucible of a heating stage built for an optical microscope (TS1500EV-6, Linkam Scientific Instruments Ltd, UK). The heating stage was then used to control the sample temperature with an accuracy of better than 1 °C, while the sample could be monitored with a microscope-based Raman spectrometer system (single monochromator Jobin-Yvon, Edison, NJ). For the experiments reported here, the Raman spectra were excited with a 514.5 nm laser (Coherent, Santa Clara, CA). From the Raman spectra, the fraction of monoclinic and tetragonal zirconia at a given time could be determined directly. The advantage of this technique is that the Raman signal from both monoclinic and tetragonal phases is very strong. This enables short (2–4 s) collection times in comparison with the timescale on which the phase transformation occurs (tens of seconds to hours) or the time needed for a typical X-ray diffraction pattern (hours). Furthermore, the Raman spectra originate from the full thickness of the coating, whereas X-ray diffraction is limited to the top $\sim$9 µm (for Cu $K_{\alpha 1}$ X-ray).

In preliminary experiments, the sample was continuously heated at a rate of 130 °C min^{-1} from room temperature to 1200 °C, and then continuously cooled at the same rate back to room temperature. Raman spectra were collected every 10 s, to monitor the evolution of the monoclinic and tetragonal phases.

The sequence of the main experiments is shown schematically in Fig. 3. The sample was first heated at 600 °C ("A" in Fig. 3). This value was chosen because at this temperature, as will be shown in the following section, the coating fully and quickly transformed to the tetragonal phase, regardless of the initial state. Then the sample was cooled to room temperature at a rate of 130 °C, enabling the coating to retain the tetragonal form. Finally, the temperature was raised to a value between ambient and 375 °C