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In-situ investigation of martensitic transformation toughening with electron backscatter diffraction and nano-indentation

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ABSTRACT

Quantitative and direct evidence for tetragonal to monoclinic martensitic transformation toughening was revealed by electron backscatter diffraction (EBSD) and in-situ nanoindentation, using plasma-sprayed 3 mol% Y_2O_3–ZrO_2 coatings. On the basis of EBSD phase distribution, four zooms with different phase compositions and microstructure were selected. The tetragonal grains, which were surrounded by large pores, completely transformed into a monoclinic phase, but were then crushed when subjected to a loading of 10 mN. Moreover, the critical excitation stress σ_c for the martensitic transformation was estimated to be about 4.2 GPa. According to the displacement curves, the ratio of reduced modulus to hardness (E_r/H), which directly indicates the toughness of a material, was quantitively calculated. This experimentally demonstrated that both the elastic and plastic deformation capacity of the partially transformed grain were significantly improved, compared with the untransformed tetragonal grains. These findings will provide a fundamental insight into martensitic transformation toughening.

1. Introduction

Zirconia exists in three crystallographic phases: cubic *C* (*Fm3m*, $t > 2640$ K), tetragonal *T* ($P4_2/nmc$, 1430 K $< t <$ 2640 K), and monoclinic *M* ($P2_1/c$, $t <$ 1430 K) [1]. Generally, by alloying with Y_2O_3, the metastable tetragonal phase can be obtained at room temperature, which is widely used as a thermal barrier coating (TBC) [2,3]. Especially, the *T* to *M* phase transformation of zirconia has been recognized as a 'martensitic transformation,' which is defined as a displacive structural transition and which exhibits lattice invariant strain and can effectively improve the fracture toughness [4,5].

The crystallographic characteristic during the *T* to *M* transformation, such as the orientation correspondence and monoclinic growth modes, have been successfully anticipated using phenomenological theory, and experimentally observed using transmission electron microscopy (TEM) [6], atomic force microscopy (AFM) [7] and X-ray diffraction [8]. Especially, electron backscattered diffraction (EBSD) has recently been reported as a powerful tool for the analysis of the crystallographic orientation and monoclinic variant configuration with an angle resolution of 0.1° and a spatial resolution of about 50 nm [9]. This is mainly due to the fact that the *T* to *M* phase transformation generally occurs in single or several grains with a size in the order of tens of nm [10]. Additionally, the transformation may be completely or partially transformed.

However, the experimental characterization of monoclinic transformation toughening has been one of the main challenges regarding the attaining of a comprehensive understanding of *T* to *M* martensitic transformation. Although efforts have been made to predict the shape strain, nucleation strain, or net transformation strain based on the outputs of phenomenological theory [11], the theory addresses purely mathematical aspects and not physical or chemical terms [12]. Moreover, the phase component was also used to evaluate the effect of toughening on crack propagation. Danied et al. and Xue et al. [13] argued that the existence of monoclinic phases could improve the fracture toughness of zirconia ceramics, as measured by the Vickers indentation or R-curve methods. However, a conventional toughness characterization would be ineffective for evaluating the transformation toughening, given that the transformation occurs at the nano-scale.

Recently, in-situ nanoindentation and a focused ion beam were successfully used to induce martensitic transformation in machined pillars [14–16]. However, most of this research has focused on the shape memory of the ZrO_2 martensitic transformation. Transformation

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toughening has seldom been mentioned, due to the absence of in-situ phase identification. Thus, to date, very little direct and quantitative experimental evidence of transformation toughening has appeared in the literature.

Considering transformation toughening, the preparation of a specific ceramic sample was also difficult because there is no guarantee that spontaneous transformation would occur during the sintering. Consequently, the martensitic transformation was usually induced by thermal treatment in water vapor with zirconia ceramics. Fortunately, plasma spraying is very similar to the quenching process used for steels, because the powders are melted and accelerated in the plasma torch, after which they collide with the substrate where they rapidly solidify. However, although there has been considerable research addressing the reduction of the thermal conductivity and increasing the thermal stability of TBC, relatively few studies have attempted to understand the tetragonal (*T*) to monoclinic (*M*) phase transformation and transformation toughening [3]. The main reason for this is that the associated volume expansion of 4–5% would lead to a degradation of the TBC. On the other hand, however, this opens up new opportunities for the investigation of ZrO_2 martensitic transformation toughening.

In the present study, first, the phase identification and orientation relationship of martensitic transformation in plasma-sprayed YSZ coatings was investigated and analyzed by EBSD. Subsequently, according to the phase composition of the untransformed and partially transformed grains, in-situ nanoindentation in a focused-ion beam (FIB) was employed to measure the hardness, as well as the Young's modulus. Thus, the effect of martensitic transformation toughening was quantitatively and directly evaluated.

2. Experimental methods

A Metco A-2000 atmospheric plasma spray system with an F4-MB plasma gun (Sulzer Metco AG, Switzerland) was used to deposit the 3 mol% Y_2O_3–ZrO_2 thermal-barrier coatings. Based on the results of our previous study [3], the main plasma spray parameters were set as follows: the current was 600 A, the Ar gas-flow rate was 69 L/min, the H_2 gas-flow rate was 35 L/min, and spraying distance was 12 mm. This improved the melting and the velocity of the powder.

X-ray diffraction (XRD) analyses were performed using a Bruker D8 Advance X-ray diffractometer using Cu Kα radiation at 40 kV and 40 mA. To prepare the sample for EBSD characterization, it was first subjected to mechanical polishing, followed by ion-beam polishing. The primary EBSD data were acquired using an FEI Magellan 400 scanning electronic microscope, equipped with an Oxford EBSD system. It is known that zero solutions should not be used during noise-reduction processing. In the present work, isolated points that were incorrectly indexed (i.e., wild spikes) were removed, after which compensation was applied based on the six neighboring points.

To investigate the effect of transformation toughening, special zooms with partially transformed and untransformed grains were accurately chosen to measure the local mechanical properties of the sample, using in-situ nanoindentation. Indentation was performed using a constant loading rate of 0.2 mN/s, with a hold time of 10 s. The maximum load applied with the indenter was 10 mN.

3. Results and discussion

3.1. Phase distribution of coatings

The cross-section morphology of the polished coatings is shown in Fig. S1. The plasma spraying inevitably produced coatings containing many pores and cracks. Such defects would result in scratches when the sample was prepared by ion-beam polishing, as shown in Fig. S1. An EBSD analysis was performed at the sample position shown in Fig. S1. The band contrast map, which indicated the diffraction pattern quality and points to a satisfactory indexing rate of about 85%, was shown in Fig. 1(a). The remaining unindexed points were mainly due to the topography associated with the pores and cracks. In particular, zoom 1, indicated by the arrows in Fig. 1, could be used to confirm the location and further perform nanoindentation, which will be discussed in detail later.

In Fig. 1(b), the red regions correspond to the tetragonal phase, while the yellow areas can be attributed to the monoclinic phase. The total volume fraction of the monoclinic phase was found to be 5.2%. The existence of the monoclinic phase could be also confirmed by the XRD data, as shown in Fig. 2.

Four specific zooms, which avoided the influence of pores and cracks, were chosen for the nanoindentation experiments, as shown in Fig. 1 and S1. According to the local phase distribution shown in Fig. 1(b), zoom 1 to zoom 3 were the untransformed tetragonal regions, while zoom 4 was a partially transformed tetragonal grain. Especially, zoom 1 and zoom 3 were all untransformed regions composed of several tetragonal grains. However, the surroundings of zoom 1 were more incompact than those of zoom 3, because it was mainly wrapped by the large pores and non-melted powders. Zoom 2 was one large tetragonal grain with the size of 10.6 μm.

The Euler map and pole figure for the close-up of zoom 4 are shown in Fig. 3. Only one monoclinic plate could be distinctly found within its parent tetragonal grain. Based on a pole figure analysis, their orientation relationship was an atypical correspondence where the $(100)_m$ planes were parallel to the $(001)_t$ planes (as marked by the squares), and the $(010)_m$ and $(001)_m$ planes were parallel to $\{110\}_t$ (as marked by the circles and triangles). This was consistent with the findings of our previous study [10].

3.2. Stress-induced martensitic transformation

A load of 10 mN was applied to zoom 1, and the load–displacement curve was as shown in Fig. 4. In particular, two large strain plateaus could be clearly observed, which directly indicates the occurrence of the stress-induced martensitic transformation and the motion of the tetragonal-monoclinic interfaces. This was consistent with the results obtained by Du [14]. After unloading, the substantial residual displacement, which corresponded to the unrecovered deformation, could also be clearly observed in Fig. 4.

According to the EBSD mapping shown in Fig. 1, zoom 4 could be treated as an isolated pillar, which was made up of several isometric tetragonal grains and surrounded by large pores and cracks. Consequently, a simple point-loaded cantilever beam model could be used to estimate the compressive strain on the surface of zoom 4, according to the report of Du [14], where also stated that the martensitic transformation was also induced by nanoindentation. The effective size of the pillar was about 11.9 μm, and the maximum displacement (as the first plateau) applied in zoom 1 was about 1250 nm. Thus, the strain was equivalent to about 10.5%. Using the values obtained by Shinmi et al. [17], the elastic modulus was about 40 GPa. As a result, the critical compressive stress σ_c for the stress-induced martensitic transformation could be estimated at about 4.2 GPa at room temperature. It is worth to mention that there were also small fluctuations in the loading curve (Fig. 4), which might be caused by the pores and cracks in coatings. Generally, it could be ignored, comparing with the large displacement of two strain plateaus.

A more detailed comparison of the morphology was shown in Fig. S2. It was clear that zoom 4 was crushed after the measurement of the nanoindentation. In addition, further evidence of the martensitic transformation was also provided by EBSD phase analysis, which was conducted in-situ after the measurement of the nanoindentation. As shown in Fig. 5, most of the tetragonal grains in zoom 1 disappeared, and the three remaining grains could all be accurately indexed by the monoclinic phase, as indicated by the arrow.