ESRF	**Experiment title:** Strain and the nucleation of the monoclinic phase in the near-surface region of yttria-stablized zirconia	**Experiment number**: ME1153
Beamline: ID31	**Date of experiment**: from: 6.7.05 to: 11.7.05	**Date of report**: 2.9.05
Shifts: 17	**Local contact(s)**: Michela Brunelli	*Received at ESRF:*

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Report:

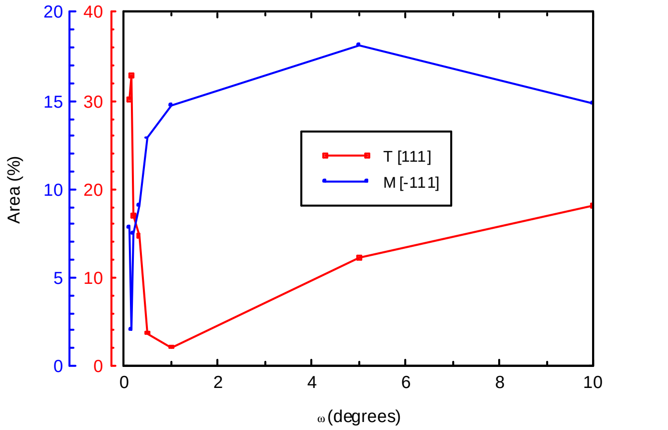
Because of its outstanding fracture toughness and fracture strength at room temperature, yttria stabilized tetragonal polycrystalline zirconia (Y-TPZ) has been increasingly used in human body articular implants for almost two decades. Nevertheless, alarming problems related to in-service failure of zirconia have been reported[1], and firms distributing orthopaedic implants have recalled Y-TPZ hip prostheses due to an episode of fractures of zirconia ceramic femoral heads.

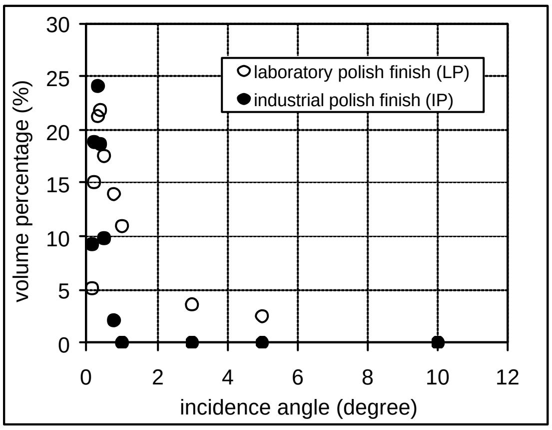
Different models have been proposed to explain this low temperature degradation (LTD). In all of these, the roles of the water molecule and internal stresses are emphasized[2,3,4,5], but the real mechanism has yet to be confirmed. The fundamental cause of degradation is the tetragonal to monoclinic phase transformation, which a recent investigation has shown to occur via a nucleation and growth mechanism[4,6]. Observations have shown that LTD begins via the transformation of one or a few grains, and then propagates from the initially transformed grains to their neighbors, because of the formation of stresses and microcracks around them.

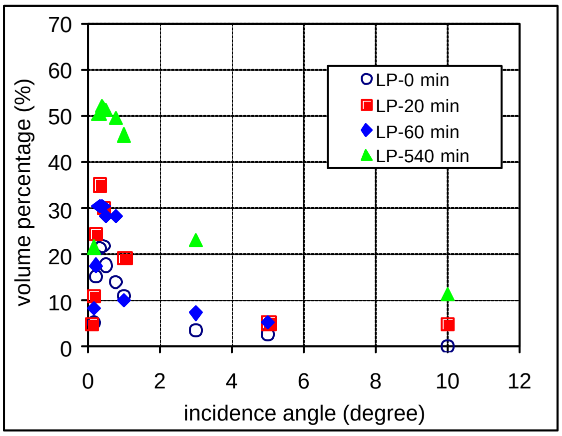
We have used beamline ID31 to perform high resolution parallel beam powder diffraction measurements at grazing incidence to probe the strain and phase composition below the polished surface of Y-TZP ceramics. Unlike alumina, in polished and aged Y-TZP, microstrain and diffracting domain size broadening of the Bragg peaks is not observed in the peaks associated with the tetragonal phase. There is **narrowing** of the Bragg peaks from the monoclinic phase in the near surface region. The fraction of monoclinic to tetragonal phase goes down very near to the surface (fig 1.). Our data show that the final polish has left surfaces, finished by either industrial or laboratory methods, still containing significant amounts of the monoclinic zirconia phase up to 24 vol% within a near-surface layer of about 200 nm, followed by a decrease with depth (fig. 2). When the polished surface was aged in an autoclave at 123°C under a water vapour pressure of 1.3 bar, we found that the amount of monoclinic phase increased with ageing time and followed a very similar pattern of falling with depth after a maximum m-ZrO_2 content of >50 vol% (fig. 3). These results show that, for polished surfaces, nucleation of the monoclinic phase was not required for ageing to occur; such nuclei were already present on the very top surface.

The associated surface strain on the polished surface appears to be much more complicated than that we observed in alumina and alumina/silicon carbide nanocomposites[7,8]. It has been found that the majority of the residual strain existed inside a “deformed zirconia” phase or a possible rhombohedral phase[9,10]. The amount of this phase in the polished surface reached up to more than 50 vol% with a substantial peak broadening, largest at the surface and

reducing with depth (fig. 4). We found that the increase in the monoclinic phase during ageing was accompanied by a reduction of the "deformed zirconia", but little change in the strain damage profile (i.e. FWHM) in the near surface. This suggests that the monoclinic phase is transformed from the "deformed zirconia" rather than the unstrained t-ZrO_2. We have the first experimental indication that the as-polished surfaces already possess conditions necessary for the martensitic transformation of zirconia to take place. However, we do not know what would happen if the residual monoclinic phase and the "deformed zirconia" were controlled through post-polish treatments. We have not yet identified the structure of this "deformed zirconia" or how it has been formed.







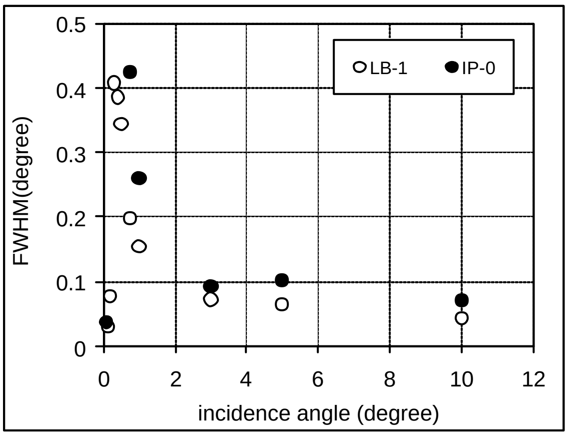


Fig 1: Variation of vol % monoclinic and tetragonal phases (Bragg peak area) in Y-TZP as a function of incidence angle (proportional to depth probed) in a ground and aged sample

Fig 2: Depth distribution of near surface m-ZrO_2 in polished Y-TZP.

Fig 3: Depth distribution of m-ZrO_2 in the near surface of polished Y-TZP after aging for different times

Fig 4: Variation of FWHM of deformed zirconia with incidence angle.

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