SAM/AES Analysis of Grain Boundaries in Zirconia Ceramics

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Introduction

The local information about the distribution of non soluble compounds such as silica and alumina in the grain boundaries of zirconia as well as the distribution of the soluble stabilising metal oxides enables the ceramic scientist to tailor their functional and structural properties. The aim of this study is to investigate grain boundary impurity silicate phases and the segregation process of cations in zirconia ceramics using SAM/AES.

Experimental

The maps of the elemental distributions were obtained using the field emission based Perkin Elmer PHI-670 Scanning Auger Nano-probe. The lateral resolution was better than 40 nm. The depth profiles on titania-stabilised zirconia ceramics were performed with a PHI Model 4300 SAM spectrometer. The sample was heated to 450°C by resistivity in order to enhance the ion conductivity of the ceramic material.

Results and Discussion

Grain Boundary Analysis of the Yttria-stabilised Zirconia Ceramic (Y-TZP) with Silica and Alumina Impurities

Secondary electron image of the Y-TZP sample

Aluminum (KLL) Auger image of the Y-TZP sample

Silicon (KLL) Auger image of the Y-TZP sample

Zirconium (LMM) Auger image of the Y-TZP sample

Silica and alumina are wetting the adjacent borders of the grains. The distribution of the Zr(LMM) Auger image is complementary, filling the space left by the other two compounds.

AES surveys of the Y-TZP sample

In all three spectra the Si(KLL) and the Al(KLL) transitions are visible while for alumina only the Al(KLL) peak at higher kinetic energy is shown. Taking into account the difference in the escape length for electrons of an energy less than 100 eV and of an energy around 1400 eV the alumina containing silica layer appears to be covered by a silica overlayer of a thickness between 2 and 7 monolayers.

The Si(LMM) Auger transition indicates a higher concentration of silica at the triple point by a factor of 1.15, while the Si(KLL) Auger transition shows a concentration 2 times as high. Since the relative Al-concentration does not vary at the investigated points, the silica content must be higher at the triple point than at the grain boundaries.

Depth Profile Analysis of Ti-stabilised Zirconia Ceramic

Secondary electron image of a Ti-zirconia sample

The grains of the intergranularly fractured surface show faceted grain boundary surfaces due to the twin structure resulting from the tetragonal to the monoclinic phase transition.

The concentration of the doping ions was constant at several intergranularly fractured grains.

AES depth profile of the Ti-zirconia sample recorded at the area shown in the SEI

The Ti-concentration profile shows an increase of the titanium cation concentration towards the near-grain-boundary. After sputtering to a depth of 3 nm, titanium reached the bulk level of 12.3 cat% which corresponds to 12.3 mol% titania, as it was determined by chemical analysis. At the fracture surface, the titanium concentration of 47 cat% is by a factor of 3.8 higher than in the bulk.

Despite this segregation, the four valent titanium-stabilised material shows very pronounced grain growth in contrast to the three valent dopants present in zirconia ceramics. The Ti-enrichment might, therefore, rather be present in a very thin glassy film of about 1 to 3 nm thickness at the grain boundaries.

Conclusions

Auger analysis can be performed at high resolution on insulating zirconia ceramics by preparing specimens smaller than the penetration depth of the probing electrons or taking advantage of the ion conductivity of the material.

An alumina rich glassy silicate phase was found at the zirconia grain boundaries and at triple points. From the analysis of the KLL and LMM Auger transitions for aluminium and silicon, it was concluded that the alumina enriched phase is covered by at least 2 monolayers of silica. This observation was affirmed by XPS depth profiles on intergranularly fractured surfaces.

Zirconia ceramics doped with 12.3 mol% titania were investigated using SAM/AES in combination with ion sputtering. The titanium ions were found to be enriched by a factor of 3.8 in the outermost layers of the grain surface.

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