Table 2. O contents and AES results for Si_3N_4 ceramic powders.

No.	Type/origin	O content (wt %)	area	O/N (at.) point analysis	d^a nm	-O/N (d) ^b
1	LC12/H. C. Starck	1.3	0.28	0.11 ± 0.02	(9) ^c	no ^c
2	SNB/Denka	2.7	0.83	0.51 ± 0.10	38	yes
3	SN9FW/Denka	0.7	0.07	0.13 ± 0.04	16	yes
4	SNE10/Ube	1.3	0.60	0.13 ± 0.07	7	yes
5	A200/Toshiba	2.2	0.40	0.14 ± 0.14	8	yes

^a Reference^b: $\text{Ta}_2\text{O}_5/\text{Ta}$.^b Distinct O/N decrease with depth.^c Only a slight decrease of the O/N ratio from 0.098 ± 0.002 at $d = 0$ nm to 0.063 ± 0.025 at 18 nm was observed.**Table 3. Main constituents of NBS 1633a coal fly ash.**

Element	Ca	Fe	K	Si	Al	O	S
wt % ^a	1.11	9.40	1.88	22.8	14 ^b	— ^b	— ^b
at. % ^c	1	5	1	25	16	52	—
Grain 1 ^d	3	28	1	15	15	38	0
Grain 2 ^d	2	9	1	30	23	33	1

^a As certified.^b Not certified, Al value given for information.^c Recalculated.^d Rounded mean at.% between 30 and 70 nm (ref. $\text{Ta}_2\text{O}_5/\text{Ta}$) by AES point analysis.

smaller than area ones, which might be due to hydroxyl condensation or O diffusion under intense irradiation. Sample no. 1 might show the limits of the method, because no distinct depth profile could be attained starting with an O/N ratio of 0.1.

Environmental analysis: rivulet sediments and coal fly ash. The main question as to whether different chemical compositions and depth profiles between different grains could be attained, can be positively answered: as for the sediment, a C-rich layer of about 10 nm thickness covers inorganic oxidic substances containing different Al and Si concentrations (20 to 40%). Differences were also seen for the minor constituents K, Ca, and Fe (all between 0 and 4%), which were enriched at the surface or covered by the C-layer and/or distributed homogeneously in greater depths (≤ 100 nm). Similar qualitative observations

could be made on coal fly ash for which specified and found contents are listed in Table 3. No elements with percentages below 1 could be detected, except P (in a surface or intermediate layer) and S, both not specified.

CONCLUSION

In spite of the main limitations (beam drift, particle size and applicable beam current (charging)) there is still enough space for AES measurements on poorly conducting particles. However, these measurements are tedious because of manual drift corrections and delays after sputtering, and because large amounts of particles must be analysed to obtain quantitative results. Therefore, automatic image shifts compensating for drifts and more sophisticated techniques of sample preparation (dense monolayers of non-agglomerated particles) are required.

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Microstructure of Fe Implanted Yttria Stabilized Zirconia Studied by Mössbauer Spectroscopy and TEM

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INTRODUCTION

The solid solutions of zirconium and yttrium oxides, $(\text{ZrO}_2)_{1-x}(\text{Y}_2\text{O}_3)_x$, abbreviated ZYx.100, are well known high temperature oxygen-ion conducting solid electrolytes and are

used in applications like oxygen sensors, oxygen pumps and fuel cells.¹ For these applications an electronically conducting electrode material on top of the solid electrolyte is necessary. Conventionally porous noble metal (Pt) electrodes are used, but mixed (electronic and ionic) conducting materials are applied too.²⁻⁴ Such a mixed conducting layer can also be

obtained by implantation of a suitable ion. Top layers formed by implantation have the advantage that they can be made very thin and that no sharp interface exists between the top layer and electrolyte. The electrochemical^{5,6} and other properties depend on the microstructure of the implanted layer which is discussed here.

EXPERIMENTAL

Both single crystal and ceramic ZY17 was implanted with high doses of Fe (2 and 8×10^{16} Fe cm⁻² at 15 keV and 8×10^{16} Fe cm⁻² at 110 keV) at the Laboratory for General Physics (L.A.N.) of the State University of Groningen. Chemically prepared ZYFe10 (ZY17 containing 10 mol% Fe₂O₃) samples^{5,7} were used as comparison in the Mössbauer experiments. The microstructure was studied with a Jeol-200 CX microscope on samples thinned by ion milling. The implantation profiles were measured at the RBS facility of the L.A.N. The structural disorder introduced by the implantation in single crystal ZY17 was investigated with channelling experiments. The charge and environment of the implanted Fe was probed with conversion electron Mössbauer spectroscopy (CEMS). The integral CEMS mode was used and samples were coated with a 20 nm thick carbon layer to avoid surface charging. A detailed account of the Mössbauer experiments will be published separately.⁸

RESULTS AND DISCUSSION

The shapes of the concentration profiles of Fe did not change during thermal treatments up to 900°C.⁹ TEM observations on as-implanted high dose samples (8×10^{16} Fe cm⁻²) showed the formation of a granular substructure, with crystallites of 30 nm, within the original grains (grain size ≥ 0.5 micron). Diffraction patterns of these grains show, in addition to the cubic ZY, also the reflections of Fe₂O₃. All reflections appear as diffuse rings indicating that both the ZY and Fe₂O₃ are fine grained and randomly oriented. Dark field images of the Fe₂O₃ reflections show very fine grained precipitates (<5 nm) dispersed through the matrix. These precipitates seem to grow with a heat treatment at 1100°C (30 min).

Combination of RBS and channelling experiments on implanted ZY17 single crystals showed that annealing up to 800°C does not restore the ordering in the Zr sub-lattice. Together with the TEM results this indicates a recrystallization of the single crystalline matrix in a random way. For polycrystalline samples it was found that in the Rutherford backscattering spectrum the step height at the oxygen edge decreased after Fe implantation. After oxidation at 400°C it increased again, indicating loss of oxygen during implantation.

Transmission Mössbauer spectra were made of 'standard' ZYFe10 samples of known Fe concentration and microstructure.¹ Besides the doublet (isomer shift, $I.S. = 0.23$ mm s⁻¹ and quadrupole splitting, $Q.S. = 1.24$ mm s⁻¹) another slight adsorption at -4.3 and 5.0 mm s⁻¹ was observed. These peaks are part of a sextuplet originating from Fe₂O₃ particles larger than 10 nm.¹⁰ The conversion electron Mössbauer spectra (CEMS) of the ⁵⁷Fe implanted materials are very complex. The spectra for annealed samples gave $I.S.$ values comparable to that of ZYFe10, indicating that all of the iron is present in the Fe³⁺ state. Computer fits with only one Fe³⁺ site all yielded systematic deviations. Better fits were obtained assuming two types of Fe: Fe_s³⁺ ($I.S. = 0.24$ – 0.25 mm s⁻¹, $Q.S. = 1.43$ – 1.48 mm s⁻¹) and Fe_h³⁺ ($I.S. = 0.24$ – 0.25 mm s⁻¹, $Q.S. = 0.86$ – 0.90 mm s⁻¹). These doublets are ascribed to Fe³⁺ substitutionally incorporated for Zr⁴⁺ (Fe_s³⁺) and very small Fe₂O₃ precipitates (<5 nm), Fe_h³⁺. The Fe_h³⁺ component is also found in MgO implanted with Fe¹¹ and is

explained by the occurrence of super-paramagnetism in Fe₂O₃ particles smaller than 10 nm.^{10,12}

The as-implanted spectra could be described using this model and two additional doublets and a sextuplet. Of the extra doublets one has been ascribed to Fe²⁺ ($I.S. = 0.91$ mm s⁻¹, $Q.S. = 2.01$ mm s⁻¹), the other ($I.S. = -0.07$ mm s⁻¹, $Q.S. = 0.45$ mm s⁻¹) to iron dimers.¹¹ The additional sextuplet was ascribed to relatively large iron particles. Annealing the as-implanted samples at 300–400°C results in rapid oxidation of all iron to Fe³⁺, which is in agreement with the observed increase in the oxygen content (RBS) and strong changes in the electrical properties.⁶ The relative abundance of each Fe oxidation form could be calculated from the CEM spectra. Using the Fe depth profiles (RBS) a (metastable) solubility level of 4 – 5×10^{21} Fe cm⁻³ could be calculated. This is about the same as found for the chemically prepared samples and is about 3 to 4 times higher than the equilibrium solubility.⁷

CONCLUSIONS

The high dose implantation of Fe in ZY17 single crystals results in a random recrystallization of the surface layer. In implanted polycrystalline material an intergranular substructure is observed. In the as-implanted state metallic particles, Fe⁰ dimers and Fe²⁺ and Fe³⁺ ions are found, their relative abundance depending on the implantation conditions. After a short anneal at 400°C all these different oxidation states are rapidly converted to Fe³⁺. The maximum implanted Fe³⁺ concentration that remains (metastable) on the substitutional Zr⁴⁺ lattice sites, after a 30 min anneal at 400°C, is 4 – 5×10^{21} Fe cm⁻³, the same as found for chemically prepared ZYFe10. Annealing higher dose implantations leads to the exsolution of dispersed and very small (<5 nm) hematite particles.

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