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Detection of carbon residue on the surface of 3Y–ZrO_2 powder and its effect on the rheology of the slip

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Abstract

The surface composition and rheology of two yttria doped zirconia powders (3Y-ZrO_2) were investigated in aqueous suspensions using electron spectroscopy for chemical analysis (ESCA), infrared spectroscopy, potentiometric titration, electrophoretic mobility, and rheological measurements. Both physisorbed and chemisorbed carbon were detected on the surface of powders in different extent. The point of zero charge being different from the isoelectric point (iep) indicated the effect of carbon on the surface charge and likely the specific adsorption of cations inside the slipping plane. Infrared spectroscopy detected both physisorbed and chemisorbed carbon on the surface. Chemisorbed carbon also affected the rheology of the slips especially in acidic suspensions. Contact angle and surface energy measurements showed that powder with chemisorbed carbon has low surface energy and exhibited a hydrophobic surface.

Keywords: A. Powder; B. Surface; D. Zirconia; D. Carbon; Rheology; Slip; 3Y-ZrO_2

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1. Introduction

Yttria doped tetragonal zirconia polycrystals (3Y-TZP) have attracted considerable attention for their superior mechanical properties such as bending strength and fracture toughness [1,2]. These mechanical properties depend on the uniformity and the control of microstructure. One way to produce ceramics with controlled microstructures is slip casting techniques, which have received increasing attention [3,4]. Processing of the slip from fine powders is based on colloidal processing in which the surface chemistry is of great importance.

There are various ways to manipulate intentionally the surface chemistry of powders to meet the processing demands such as free flowing behaviour, processing of soft agglomerates or agglomerate free powders [5]. Frequently the reason for changes in surface properties or behaviour of powder is the impurities, which are attached to the surface. High quality, fine zirconia powders are usually obtained by wet chemical processing, in which hard agglomerates are likely to be produced. In order to avoid hard agglomerates [6,7], for example alcohol washing is widely practiced on powders [8], in order to remove the water from the precipitated cake [9]. This treatment may lead to excess carbon residue on the surface. Carbon on the surface of powders can also originate from a faulty powder processing, which may occur in the coprecipitation of 3 mol% yttria with zirconia. Taha et al. [10] found 0.5 wt% carbon residue on the surface of such powders. Carbon as a surface impurity can affect most components at the surface of zirconium hydroxide, including free water, chemically coordinated water, and non-bridged OH^- [7]. Surface related properties of powders such as surface energy, contact angle and rheology are influenced by residual carbon and these properties can give preliminary information of the existence of the residual carbon on the surface [11,12].

In this study, the presence and role of residual carbon was investigated on the surface of zirconia powders. Two different 3Y-ZrO_2 powders that had almost identical chemical composition showed different surface related properties. The differences in these properties were mainly attributed to the amount and nature of carbon residue on the surface of powders.

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2. Materials and experimental procedure

Two yttria doped zirconia powders with 3 mol% yttria, denoted as Y3 and Y3U, were supplied by Zirconia sales UK. Tables 1 and 2 present the characteristics of the powders. Bulk chemical analysis of the powders was obtained by X-ray fluorescence spectroscopy (XRF). Quantitative analysis of carbon was carried out by heating powders up to 1000°C and using a mass spectrometer with calibrated CO and CO_2 responses to calculate the quantity of carbon.

The sessile drop method was used for determining the contact angle and surface energies of powders. Videotape recording of contact angles of known liquids was used to determine and calculate the surface energies, using the Kaelble plot (geometric mean method) [13]. Infrared spectroscopy (Perkin–Elmer FTIR 1725X) was used to detect the different bonding energies of carbon on the surface. Rheological behaviour of the slips was studied by a concentric cone and plate rheometers (Bohlin VOR and Bohlin 88) in steady shearing mode, at room temperature.

Several surface characterization techniques were used for this study. Electron spectroscopy for chemical analysis (PHI ESCA 5400) was used to determine the surface chemical composition. Surface charges and the point of zero charge were measured by potentiometric titrations (SM Titrino 702), using 0.1 M HCl, 0.1 M NaOH and 0.1 M KCl as acid, base and electrolyte, respectively. Zeta potential was measured by Electrokinetic Sonic Amplitude (ESA) in diluted suspensions and 0.01M KCl was used as electrolyte (Matec ESA 8000). Phase composition was measured by X-ray diffraction technique (XRD) using Cu K_α radiation (Siemens D500, Germany). The powder with finer particle size Y3U, was also investigated by transmission electron microscopy (TEM), (JEOL JEM 2010) to get more information of the carbon layer.

Table 1
Characteristics of yttria doped zirconia powders

	Y3U	Y3
Particle size d_{50} μm	0.15	0.79
Specific surface area (m^2 g^{-1})	17.2	7
Phase composition, % m phase[a]	21.5	25.7

[a] Balance is tetragonal phase.

3. Results and discussion

3.1. Detection of carbon

The bulk chemical composition of powders (Table 2) show minor differences in the level of impurities and major elements such as yttria and zirconia. This level of difference in the amount of impurities in bulk chemical analysis does not influence the surface related properties, unless the impurity appears selectively on the surface. Carbon content of powders is low and it can well justify the presence of carbon only on the surface of powders. The amount of carbon detected in Y3U is 5 times of that in Y3, although the surface area of Y3U is about 2.5 times of that of Y3.

Surface coverage of this amount of carbon if considered only on the surface can be calculated. Each carbon atom covers 0.070 nm^2 of the surface [14]. For Y3U the specific surface area is 17.2 m^2/g, which means that 0.32 wt% of elemental carbon would cover 11.2 m^2 or 65% of the powder surface per gram, considering that all the carbon content appears on the surface as a monolayer. However, the carbon coating is not probably monolayer, uniform and dense. The microstructure of Y3U particles studied by TEM (Fig. 1) shows some disturbances in lattice lines on the surface of the particles (marked by arrows) indicating the presence of an amorphous carbon layer. Accurate knowledge of the surface coverage of the powder by carbon layer could not be obtained by TEM. Atomic force electron microscopy also failed to show the morphology of the carbon layer.

3.1.1. IR-spectroscopy

The IR spectra of Y3 and Y3U as received and washed powders are shown in Fig. 2(a). Peaks between 2360 and 1630 cm^{-1} correspond to the contamination and atmospheric CO_2, respectively [15]. The peak close to 3500 cm^{-1} is for O–H bonds. There are three peaks related to chemisorbed carbon in Y3U in the range of

Table 2
X-ray flourescence analysis for Y3 and Y3U powders

Powder	Composition wt%					
	ZrO_2 C[a]	Na_2O Fe_2O_3	Al_2O_3 Y_2O_3	SiO_2 HfO_2	P Cl	CaO TiO_2
Y3U	91.49	0.006	0.834	0.010	0.076	0.036
	0.32[a]	0.03	4.35	2.05	0.026	0.03
Y3	92.57	0.035	0.294	0.105	0.083	0.020
	0.06[a]	0.029	4.49	1.43	0.036	0.11

[a] Carbon measured by gas evolution analysis.

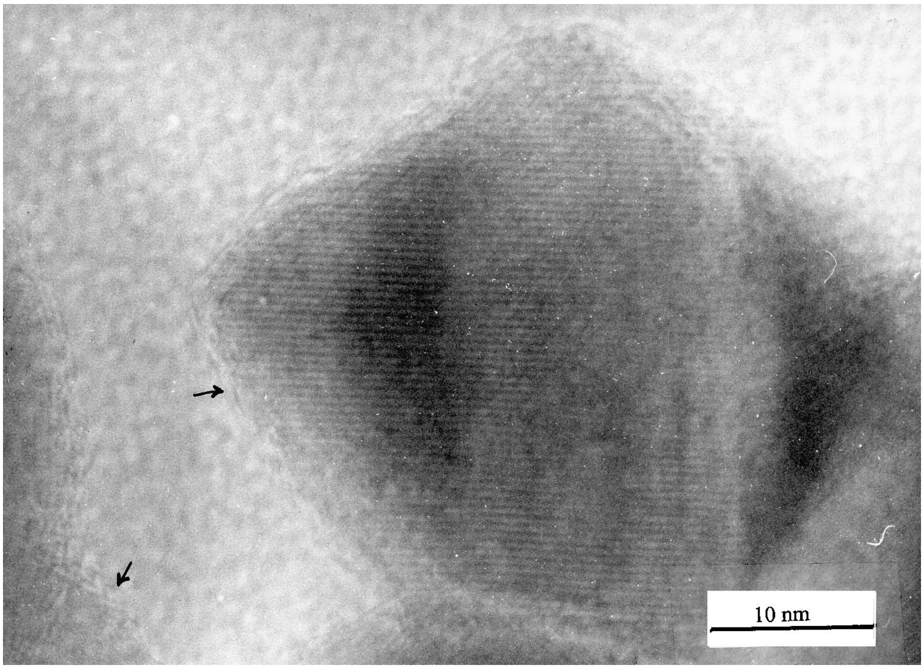

Fig. 1. TEM photo of Y3U particles.

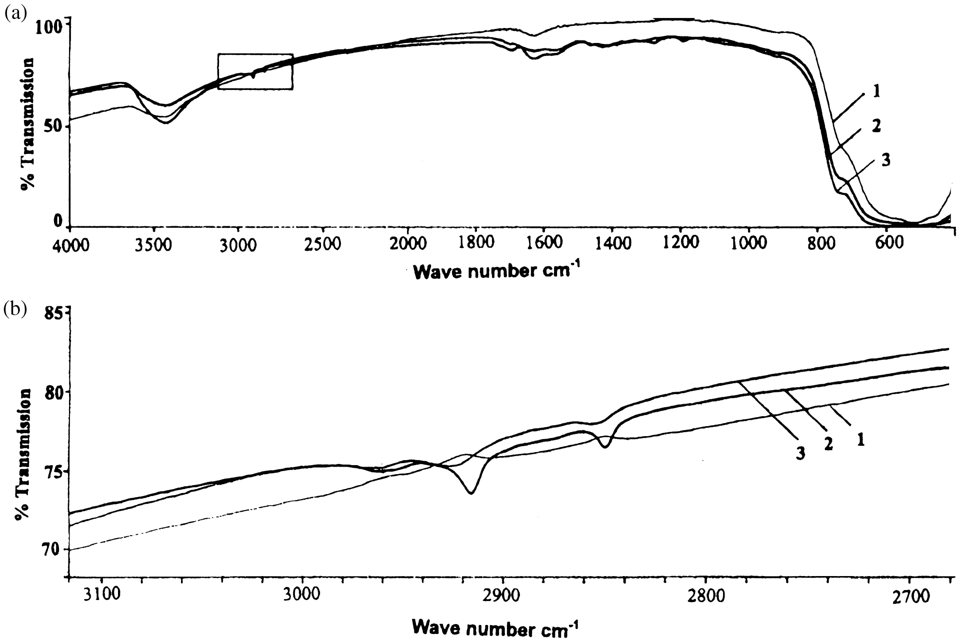

Fig. 2. IR spectra of Y3 and Y3U powders (a) and in more details at 2800–3000 cm^{-1} (b): (1) Y3 as received powder; (2) Y3U washed powder; and (3) Y3U as received powder.

2800–3000 cm^{-1} that are not present in Y3 spectrum. In Y3U spectrum, 3 peaks at 2962, 2927 and 2856 cm^{-1} correspond to the vibration stretching of the C–H and -COO–H groups. Atmospheric carbon contamination which is physisorbed can be washed away by water whereas chemisorbed carbon resists such treatment. To minimize the effect of atmospheric and physisorbed carbon, Y3U powder was washed with distilled water five times. More intense peaks of the washed powder between 2850 and 3000 cm^{-1} in zoomed area [Fig. 2(b)] confirmed the presence of chemisorbed carbon.

3.1.2. Surface analysis

The results of surface analysis by ESCA are shown in Table 3. Carbon contamination on Y3U as received powder is higher than that of Y3. There is not a significant drop in carbon level when the Y3U powder is washed. This indicates that the different levels of carbon concentration between Y3 and Y3U powders are mostly related to chemisorbed carbon. The result of ESCA curve fit for carbon peaks showed that the most intensive carbon peaks are associated with carbon-carbon or carbon-hydrogen bonding (Fig. 3) but peaks at 291 and 293 eV are more important regarding the adsorbed carbon.

3.2. Rheological properties

3.2.1. Zeta potential

Surface inhomogeneities influence the surface charge of particles in suspension. In order to understand the rheological behaviour of particles in suspensions, the surface charges of the particles were characterized in details by electerophoretic measurement and titration. Dilute aqueous suspensions of 0.05 wt% were prepared for electrophoretic measurements. Zeta potential is the surface potential of the kinetic particles at, or near to, the beginning of the diffuse double layer. The net surface charge is negative at pH > iep and positive at pH < iep. The affinity of potential-determining ions being H^+ and OH^- for ceramic oxides changes the zeta potential as a function of pH and the pH of zero potential is denoted the isoelectric point (iep) [16]. The zeta potential is measured at the slip plane that also includes the specifically adsorbed ions [17]. Fig. 4 shows the zeta potential of Y3 and Y3U suspensions. Zeta potential of Y3U is much lower than that of Y3 especially in acidic pH [18]. Iep of Y3U has shifted about 1.5 pH units towards acidic pH.

Table 3
ESCA results on Y3U and Y3 as received and washed powders sputtered for 1 min

% Atomic concentration	Zr3d	Y3d	Cls	Ols
Y3 as received	25.9	2.2	5.9	65.9
Y3U as received	24.37	2.27	10.43	62.06
Y3U washed	23.96	2.16	8.75	63.56

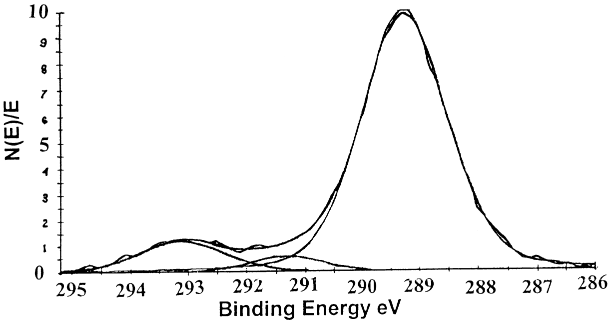

Fig. 3. ESCA curve fit for carbon peaks in Y3U (as received). The peak at 289 eV is for carbon-carbon and carbon-hydrogen bonds and the peaks at 291 and 293 eV are for different carbon–oxygen bonding.

This observation was confirmed by viscosity measurement at acidic pH. Acidic deflocculation pH is almost absent in Y3U suspension, while Y3 suspension is deflocculated in the acidic pH range. Y3 can be dispersed in both acidic and basic aqueous solutions [18].

The adsorption of water on ZrO_2 differs from that onto carbon sites [19]. In both cases two types of adsorbed water exist: physisorbed water, which can be removed by heating to 115°C and, dissociatively chemisorbed water. On ZrO_2, chemisorbed water exists as hydroxyl groups of variable thermal strength, and is gradually removed by heating up to 1000°C. Carbon surfaces retain water in the form of acidic functional groups that typically decompose upon heating below 500°C. The lower iep of Y3U can be attributed to the effect of carbon on the surface of Y3U particles due to the functional acidic groups.

3.2.2. Potentiometric titration

The number of acid and base sites on the surface (titration data) provides an estimate of the surface groups (Fig. 5). The high NaOH uptake indicates a large number of weakly acidic surface sites. Similarly the fair uptake of HCl indicates the presence of surface patches of basic character, partly associated with carbon deposits or carbon-bound oxygen. Possible sites include phenolic-type complexes bound to carbon and hydroxyl groups on zirconia.

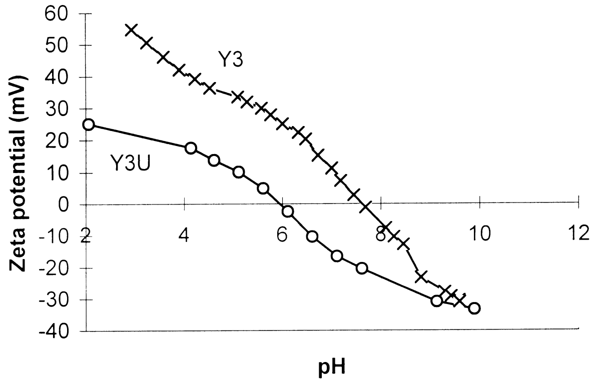

Fig. 4. Zeta potential of Y3 and Y3U powders.

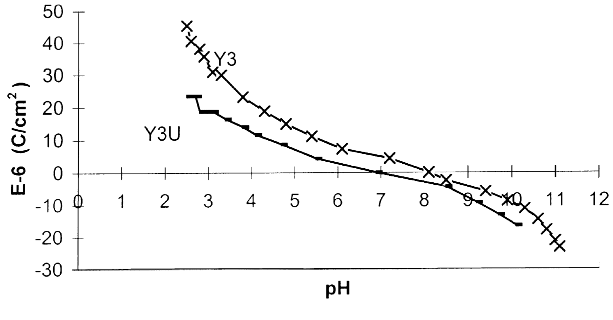

Fig. 5. Surface charge (σ_0) measurement of Y3 and Y3U by mass titration. Supernatant was used as blank.

There is a particular concentration of H^+ and OH^- for which the number of positively charged sites and negatively charged sites are equal and the surface potential is zero. This is denoted the point of zero charge (PZC). For homogeneous surfaces and if there is no specific adsorption of ions, the iep is equal to PZC. The difference between PZC and iep can be taken as a result of surface charge heterogeneity or specific adsorption. When PZC > iep it implies specific adsorption of anions and when PZC < iep specific adsorption of cations is observed [12]. Since PZC > iep for Y3U, anionic impurities seems to enrich on the external surface. This is attributed to a layer of carbon with weakly acidic oxygen functional groups. The PZC of Y3 is larger than that of Y3U but it almost equals the iep of the suspensions. The true potential determining ions in yttria doped zirconia suspensions besides H^+ and OH^- are all the ions that may desolve and readsorb on the surface such as Si, Y and Zr [20,21].

Carbon and zirconia behave amphoterically in water. At PZC, the extent of protonation of basic groups matches that of the dissociation of acidic groups, resulting in a zero net charge. The PZC, ultimately reflects the exchange of potential-determining ions throughout the wetted surface. Thus given enough time for equilibration, even the exchangeable sites located within the small pores accessible to water will contribute to the PZC. On the other hand, when an external potential is applied to charged particles in solution (as in electrophoresis), these will move according to their external electrostatic fields, to which internal pore charges are unlikely to contribute.

3.2.3. Rheology in acidic solution

Electrostatic stabilization of ceramic suspensions is accomplished in acidic or basic suspensions far enough from the iep to ensure high similar surface charges on particles, i.e. high positive or negative zeta potentials. Y3 powder was dispersed effectively in acidic pH range but for the Y3U powder no acidic range of pH was found for electrostatic dispersion. The viscosity of Y3U suspensions in acidic solution of pH 1.4 is mush higher than that of Y3 solution (Fig. 6). It is not known to what extent the carbon residue on the surface and the hydrophobicity of the surface would affect the inter-particle forces and to what extent the hydrophobic reaction between particles would dominate. To understand the rheology of Y3U, a review of the rheology of hydrophobic particles is necessary.

Hydrophobic surfaces may influence the inter-particle forces and change the rheology. The understanding of forces between hydrophobic particles may help to interpret the rheology of the suspension. An attractive force of relatively long range and of an order of magnitude stronger than the van der Waals forces has been measured between hydrocarbon surfactants adsorbed on two cylindrical mica sheets in an aqueous solution [22].

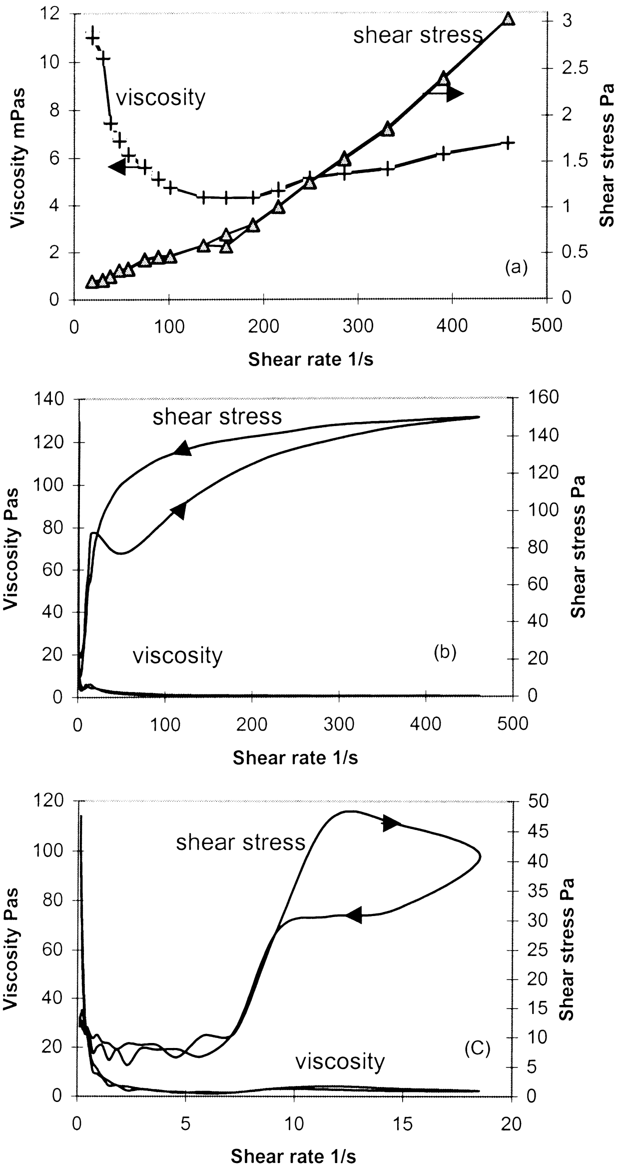

Fig. 6. Rheology of Y3 and Y3U slurries in acidic solutions at pH = 1.4; (a) Y3; (b) Y3U in the same range of shear rate; and (c) Y3U at low shear rates.

The hydrophobic force comprises two components: a short-range force in about 10 Å and a long-range component that acts at about 100 Å. The long-range component has a longer range than van der Waals forces. The origin of this force is not clearly understood. A number of possible origins have been suggested being attributed to entropic [23], van der Waals [24] and hydrodynamic effects [25], and interaction between positive and negative charge patches [26]. Leong [27] showed that the yield stress has been considerably increased with addition of sodium dodecyl sulphate (SDS) and dodecylamine (DAL) in zirconia suspensions and attributed this increase to hydrophobic interactions. The hydrophobic surfaces repel rather than attract simple ions in the solution [28].

Viscosity and shear stress were measured in acidic solution of Y3 and Y3U at pH 1.4, using steady state shearing (Fig. 6). Viscosity and shear stress are reversible as a function of shear rate in Y3 suspension. At this pH, the rheological behaviour of the Y3U slurry was different from that of Y3 slurry and there were differences in shear stress vs. shear rate behavior in different ranges of shear rate.

Small particles in contact with water may have various surface processes giving rise to electrostatic fields. Carbon and ZrO_2 both can exchange ions, protons and molecules in order to balance their respective fields [29]. ZrO_2 surfaces contain one type of dissociating group (hydroxyl) but carbons can offer at least four distinct surface groups which in addition to nonpolar regions, endow carbon surfaces with an unparalleled chemical variability. Viscosity of Y3U suspension is higher than that of Y3 and shows strong shear thinning behaviour. Higher viscosity and irreversible behavior of shear stress vs. shear rate in Y3U suspension can be attributed to the hydrophobic patches of carbon on the surface of Y3U particles. Different behaviour at low shear rates up to 30 s^{-1} and medium shear rate 30–500 s^{-1} shows the shear rate dependency of rheology at this pH. Shear stress in running down the shear rate was higher than that in upward shearing of Y3U suspension that resembles rheopexy (above 30 s^{-1} shear rate). Below 30 s^{-1} shear rate, shear stress were lower in shearing down the suspension (resembles thixotropy). The reason for this shear rate dependent behaviour is not known at the moment. Different interactions of hydrophobic carbon patches (carboxyl groups), on the surface of the particles at low and medium shear rates may result in thixotropy and rheopexy of Y3U suspension.

3.3. Surface energy components and contact angles

Surface energy components and the contact angle are monitoring the hydrophobicity and hydrophilicity of powders. Powders were washed in ultrasonic bath, dried at 120°C and pressed densely to a disk shape. The contact angle of a free flow droplet of a known liquid (sessile drop method) was video recorded in 20 ms intervals and was analyzed with an image analyzer computer program. The liquids used in this study were dimethylglycerol, glycerol, 1-bromonaphtalene, formamide and distilled water. The surface energy components were calculated from the contact angle values (Table 4).

Polar component of the surface energy is correlated to the hydrophilicity of the surface. The polar component of Y3U is lower than that of Y3. Dispersive component is correlated to the hydrophobicity of the surface and is higher for Y3U. As a result the total surface energy of Y3U is less than that of Y3 powder. The contact angle of water on Y3 is 22° and on Y3U is 39°, indicating the higher level of hydrophobicity in Y3U in aqueous solutions. This fact is justified with the presence of chemically adsorbed carbon that makes the surface more hydrophobe.

Table 4
Surface energy components and contact angles of Y3 and Y3U

	Dispersive component (mN/m)	Polar component (mN/m)	Surface energy (nM/m)	Contact angle for water
Y3[a]	21.6	41	62.6	22
Y3U[a]	22.5	32.6	55	39

[a] Measured based on geometric-mean method in ambient atmosphere at room temperature.

4. Conclusions

Carbon was detected on the surface of yttria doped zirconia Y3 and Y3U powders by ESCA and IR measurements. IR study revealed the presence of chemically adsorbed carbon on the surface of Y3U powder. TEM study on Y3U showed evidence of an amorphous carbon layer, but AFM failed to give any indication of the morphology of the layer. It is speculated that carbon is present in multilayer and nonuniform morphology. Carbon also influenced the rheology of the aqueous slip and interfered with electrostatic stabilization in acidic pH. The Y3U aqueous slip, electrostatically stabilized at low pH showed rheopexy behaviour above 30 s^{-1} shear rate and thixotropy below this shear rate. The iep and PZC of Y3U were lower than those of Y3, because of the higher carbon residue on the surface with chemical bonding. For the Y3U powder, PZC is at higher pH than iep, which implies the adsorption of anions inside the slipping plane, likely on the carbon sites.

A high contact angle for distilled water and a larger dispersive component of surface energy of Y3U powder indicated hydrophobicity, which is attributed to the presence of chemisorbed carbon on the surface.

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