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Wettability and surface free energy of zirconia ceramics and their constituents

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Measurements of contact angle for water, glycerol, formamide and diiodomethane on surfaces of zirconia ceramic stabilized with 4% magnesia, zirconia ceramic stabilized with 3% yttria, zirconia ceramic stabilized with 5% yttria, tetragonal-Y-zirconia ceramic, cubic-Y-zirconia ceramic, zirconium (IV) oxide, aluminum oxide, magnesium oxide and yttrium oxide were conducted. Using the values of contact angle, the total surface free energy of these solids, and its components resulting from different kinds of intermolecular interactions were calculated. It was found that the Lifshitz-van der Waals component of the surface free energy of zirconia ceramics only slightly depends on the amount and kind of metal oxides present in the ceramics. The acid-base component of all the studied solids is lower than 13 mJ/m^2, showing a small dependence on the kind of metal oxide. For all samples studied the electron-donor parameter of the acid-base components of the surface free energy is many times higher that electron-acceptor one. It was stated that the acid-base component probably depends on the density of OH groups on the surface of the solids studied. © *1999 Kluwer Academic Publishers*

1. Introduction

The wettability joined with the surface free energy of a solid plays an important role in many biological and technological processes [1]. The wetting of ceramics by liquid metals and alloys is a major factor controlling the effectiveness of brazing which is used extensively in the joining of ceramics [2, 3]. The wettability of molten metals against the ceramics can be predicted, among other, determining the ceramics surface free energy resulting from the different kind of intermolecular interactions. Also, the knowledge of the surface free energy of the constituents of the ceramics can be helpful to explain the possibility of their mixing in the process of ceramics formation.

Since it is not possible to measure directly the surface free energy of a solid, its determination is achieved, at present, by many indirect methods. Among other, the methods based on the contact angle measurements for appropriately chosen systems are the most popular [4–10]. One of the main problems in using these method for the evaluation of the solid surface free energy is to express the interfacial solid-liquid free energy in the Young's Equation as a function of the surface free energy of the solid and of the liquid involved.

Recently van Oss and co-workers [11–13] expressed the solid-liquid and liquid-liquid interfacial free energy as a function of the geometric mean of the Lifshitz-van der Waals components and of the geometric mean of the electron-acceptor and electron-donor parameters of the acid-base component of both phases. These expressions allow to establish the contribution of the Lifshitz-van der Waals and acid-base intermolecular interactions to the surface free energy of solids from contact angle measurements.

The main purpose of this work was the determination of the Lifshitz-van der Waals component and the electron-acceptor and electron-donor parameters of the acid-base component of the surface free energy of the zirconia ceramics and their constituents based on the contact angle measurements for water, glycerol, formamide and diiodomethane.

2. Experimental

2.1. Materials

For measurements of contact angles were used plates of zirconia stabilized with 4% magnesia, zirconia stabilized with 3% yttria, zirconia stabilized with 5% yttria, tetragonal zirconia stabilized with yttria and cubic zirconia stabilized with yttria and plates of aluminum oxide recristalized, which have been bought from Goodfellow. For contact angles measurements the powder of zirconium (IV) oxide (Goodfellow, pure $>$ 99%), magnesium oxide (Fluka, pure $>$ 99%) and discs of the yttrium oxide (Goodfellow, pure $>$ 99.5%) were also used.

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0022–2461

The powdered magnesium and zirconium oxides were pressed by means of hydraulic press to obtain discs. Details of this procedure have been presented elsewhere [14]. Then, the discs were selected by means of microscopic, and only those which showed smooth and glossy surface, without any irregularities, were used for contact angle measurements.

The following liquids were used for measurements: water, doubly distilled and deionized; anhydrous glycerol (Fluka, purity > 99.5%); formamide (Fluka, purity > 99%) and diiodomethane (Fluka, purity > 98%).

2.2. Measurements

Before the contact angle measurements the plates were washed several times in doubly distilled and deionized water, cleaned in an ultrasonic bath, dried at 110 °C for 2 h and then cooled in a desiccator with a dehydrating agent. Discs were only dried in a desiccator with a dehydrating agent for a long time.

The advancing contact angles were measured at $20 \pm 1\,^{\circ}\mathrm{C}$ by the sessile drop method using the goniometer-camera-computer system described elsewhere [15]. For a given system, the contact angle measurements were repeated several times, and the precision of the contact angle measurements was within $\pm 2^{\circ}$.

3. Results and discussion

The average values of the contact angle for water (θ_W), glycerol (θ_G), formamide (θ_F) and diiodomethane (θ_D) on the surfaces of magnesium oxide, zirconium (IV) oxide, yttrium oxide, aluminum oxide, zirconia ceramic stabilized with 4% magnesia, zirconia ceramic stabilized with 3% yttria, zirconia ceramic stabilized with 5% yttria, tetragonal (t) zirconia stabilized with yttria and cubic (c) zirconia stabilized with yttria are shown in Table I. From this Table it is seen that for a given solid the highest value of contact angle is observed for water and the lowest for diodomethane with exception of magnesium oxide. For MgO the lowest value of contact angle is measured for formamide. For polar (water, glycerol, formamide) and apolar (diiodomethane) liquids the contact angle depends on the kind of the solid studied. The lowest value of θ_W, θ_G, θ_F and θ_D were obtained for MgO and the highest for the tetragonal zirconia stabilized with yttria. Among of the metal oxides the highest values of contact angle for each studied liquid are observed for aluminum oxide.

From contact angle measurements it is possible to calculate the components of the surface free energy of a solid using the Young's equation [1]:

$$\gamma_S - \gamma_{SL} - \Pi e_L = \gamma_L \cos \theta_L \tag{1}$$

where γ_S is the solid surface free energy, γ_{SL} is the interfacial solid-liquid free energy, γ_L is the liquid surface tension (equal to surface free energy), θ_L is the contact angle and Πe_L is the pressure of the liquid film which is equal to zero for low energy solids.

TABLE I Measured values of the contact angle for water (θ_W), glycerol (θ_G), formamide (θ_F) and diiodomethane ((θ_D) on surface of ceramics and some metals oxide

Material	(θ_W)	(θ_G)	(θ_F)	(θ_D)
Al_2O_3	72.4	61.6	47.9	46.2
Y_2O_3	68.3	53.9	43	40.5
MgO	58.1	46.9	36	38
ZrO_2	71.8	54.9	44.3	40.9
ZrO_2-MgO	68.4	55.1	44	39.3
ZrO_2-$Y_2O_3^a$	66.4	51.5	39.6	40.0
ZrO_2-$Y_2O_3^b$	72.0	58	46.6	40.1
ZrO_2-$Y_2O_3^c$	74	64.9	55.7	47
ZrO_2-$Y_2O_3^d$	72.7	62.0	51.5	41.9

a—3% Y_2O_3; b—5% Y_2O_3; c—tetragonal Y-zirconia ceramic; d—cubic Y-zirconia ceramic.

According to van Oss and co-workers [11–13], for liquids and solids the surface free energy can be divided into components

$$\gamma = \gamma^{LW} + \gamma^{AB} \tag{2}$$

where γ^{LW} is an apolar component resulting from Lifshitz-van der Waals (dispersion, dipole-dipole, induced dipole-dipole) intermolecular interactions and γ^{AB} is the component resulting from electron-acceptor (Lewis acid) and electron-donor (Lewis base) intermolecular interactions.

For the γ^{AB} component of the surface free energy the following equation holds [11–13]:

$$\gamma^{AB} = 2\sqrt{\gamma^{+} \times \gamma^{-}} \tag{3}$$

where γ^{+} and γ^{-} are the electron-acceptor and electron-donor parameters of acid-base component of the solid and the liquid surface free energy, respectively.

For a solid-liquid system its interfacial free energy γ_{SL} can be expressed in the form [11–13]:

$$\gamma_{SL} = \gamma_S + \gamma_L - 2\sqrt{\gamma_S^{LW} \times \gamma_L^{LW}} - 2\sqrt{\gamma_S^{+} \times \gamma_L^{-}} - 2\sqrt{\gamma_S^{-} \times \gamma_L^{+}} \tag{4}$$

where subscripts S and L refer to solid and liquid phases, respectively.

Introducing Equation 4 into Equation 1 for $\Pi e_L = 0$, gives [11–13]

$$\gamma_L \cos \theta_L = -\gamma_L + 2\sqrt{\gamma_S^{LW} \times \gamma_L^{LW}} + 2\sqrt{\gamma_S^{+} \times \gamma_L^{-}} + 2\sqrt{\gamma_S^{-} \times \gamma_L^{+}} \tag{5}$$

Knowing the values of γ_L^{LW}, γ_L^{+}, γ_L^{-} and the contact angle for three different kind of liquids it is possible to determine the γ_S^{LW}, γ_S^{+} and γ_S^{-} values of the solid surface free energy. Generally liquids having different values of γ_L^{LW}, γ_L^{+} and γ_L^{-} and high values of their surface free energy are used for the γ_S^{LW}, γ_S^{+} and γ_S^{-}

determination on the basis of the contact angle measurements [11–13, 15]. Among those liquids water, glycerol, formamide and diiodomethane are selected.

Thus, using the γ_L^{LW}, γ_L^+ and γ_L^- values for water, glycerol, formamide and diiodomethane taken from literature [12, 16] (Table II), the γ_S^{LW}, γ_S^+ and γ_S^- values for zirconia ceramics and their constituents were calculated from Equation 5 and are listed in Table III.

As for the materials studied four liquids were used for contact angle measurements, there are four different possibilities for calculations of the γ_S^{LW}, γ_S^+ and γ_S^- values, which are denoted by three letters corresponding to the first letter of each of the three liquids employed for each combination. Nevertheless, according to our previous calculations [17] and the studies of van Oss *et al.* [12] the values of γ_S^{LW}, γ_S^+ and γ_S^- obtained from the systems of three liquids WGD and WFD are encumbered with the lowest errors, therefore, for comparison of the γ_S^{LW}, γ_S^+ and γ_S^- values between different solids only the values obtained from the WGD system, for example, will be taken into account. However it should be noted that from Table III it appears that there are considerable differences between the values of γ_S^{LW}, γ_S^+, γ_S^{AB} and γ_S for Al_2O_3 determined from the WGD and WFD, and WGF and GFD systems of three liquids, but for the other solids studied these differences are small.

Comparing the γ_S^{LW} values determined for different solids, the lowest value is for tetragonal zirconia stabilized with yttria (31.6 mJ/m^2) and the highest for zirconia ceramic stabilized with 5% yttria (36.1 mJ/m^2). However, the difference between lowest and highest values is equal only 4.5 mJ/m^2. The bigger differences between lowest and highest values are observed for γ_S^- and γ_S^{AB} for the studied solids. The highest γ_S^- values (16.4 mJ/m^2) is determined for magnesium oxide and the lowest for zirconia ceramic stabilized with 5% yttria (5.5 mJ/m^2) (Table III). The γ_S^{AB} value is the highest for MgO and the lowest for tetragonal zirconia stabilized with yttria.

TABLE II Values of the Lifshitz-van der Waals component (γ_L^{LW}), electron-acceptor (γ_L^+) and electron-donor (γ_L^-) parameters of the acid-base component (γ_L^{AB}) of the surface tension of the liquids (γ_L) taken from literature [12, 16]

Liquids	γ_L	γ_L^{LW}	γ_L^+	γ_L^-
Water	72.8	21.8	25.5	25.5
Glycerol	64	34	3.92	57.4
Formamide	58	39	2.28	39.6
Diiodomethane	50.8	50.8	0.72	0

TABLE III Values of the Lifshitz-van der Waals component (γ_S^{LW}), electron-acceptor (γ_S^+) and electron-donor (γ_S^-) parameters of the acid-base (γ_S^{AB}) component of the surface free energy (γ_S) of the ceramics and some metals oxide calculculated from Equation 5

Material	System	γ_S^{LW}	γ_S^+	γ_S^-	γ_S^{AB}	γ_S
Al_2O_3	WGF	46.96	0.05	8.03	1.24	48.19
	WGD	32.07	1.14	9.51	6.59	38.66
	WGF	32.55	1.91	7.46	7.55	40.09
	GFD	40.13	4.10	6.55	10.36	50.50
Y_2O_3	WGF	35.73	1.75	9.15	7.99	43.73
	WGD	34.95	1.87	9.24	8.38	43.27
	WGF	34.98	1.98	9.12	8.37	43.34
	GFD	35.39	2.02	7.43	7.95	43.14
MgO	WGF	34.80	2.28	16.42	12.24	47.04
	WGD	34.68	2.30	16.44	12.31	46.99
	WGF	34.69	2.31	16.42	12.32	47.01
	GFD	34.75	2.33	16.05	12.23	46.98
ZrO_2	WGF	34.56	2.12	6.59	7.48	42.04
	WGD	35.45	1.97	6.51	7.16	42.61
	WGF	35.41	1.92	6.62	7.12	42.54
	GFD	34.95	1.80	8.44	7.81	42.75
ZrO_2-MgO	WGF	36.71	1.37	9.55	7.23	43.94
	WGD	35.41	1.55	9.69	7.76	43.18
	WGF	35.46	1.63	9.49	7.86	43.32
	GFD	36.14	1.78	6.76	6.94	43.08
ZrO_2-$Y_2O_3^a$	WGF	37.98	1.69	9.58	8.05	46.04
	WGD	35.04	2.18	9.90	9.28	44.32
	WGF	35.14	2.37	9.45	9.46	44.60
	GFD	36.69	2.79	3.96	6.65	43.34
ZrO_2-$Y_2O_3^b$	WGF	37.43	1.32	5.37	5.32	42.75
	WGD	36.13	1.50	5.48	5.73	41.86
	WGF	36.18	1.57	5.33	5.78	41.96
	GFD	36.86	1.72	3.36	4.80	41.67
ZrO_2-$Y_2O_3^c$	WGF	31.85	0.73	9.74	5.35	37.19
	WGD	31.61	0.76	9.77	5.45	37.06
	WGF	31.62	0.77	9.73	5.47	37.09
	GFD	31.74	0.79	9.15	5.38	37.12
ZrO_2-$Y_2O_3^d$	WGF	35.93	0.66	9	4.86	40.78
	WGD	34.29	0.83	9.18	5.50	39.79
	WGF	34.34	0.89	8.93	5.65	39.99
	GFD	35.21	1.04	8.63	4.84	40.05

Generally, we can state that the electron-acceptor parameter is a few times lower than electron-donor one, what can suggest that oxygen plays the most important role in the values of the surface free energy of the zirconia and their constituents.

Comparing the γ_S^{LW}, γ_S^{+}, γ_S^{-}, γ_S^{AB} and γ_S values for aluminum oxide determined from contact angle measurements to those determined by "thin-layer wicking" method we can state that there are disagreement between γ_S^{LW} and γ_S^{AB} values, but the γ_S values determined by both methods are similar [18] (Table III).

Our previous studies [15] indicate that in the case of cassiterite its wettability strongly depends on the acid-base interactions resulting from the presence of OH groups and coordinate and physically adsorbed water on it. For the surface of the "dry" cassiterite its surface free energy practically results only from Lifshitz-van der Waals intermolecular interactions. Most metal oxides are hydroxylated under normal conditions, i.e., at room temperature and when water or its vapor has had access to the surface. Hydroxo-complexes of the multivalent metals are amphoteric in character; they may dissociate protons from coordinately bound water molecules or they may add protons to hydroxide ions (it is assumed that the coordination number remains constant) [19]:

$$\begin{aligned} &M^{n+}(OH)_n(OH_2)_m \\ &\quad \Leftrightarrow [M^{n+}(OH)_{n+1}(OH_2)_{m-1}]^- + H^+, \\ &M^{n+}(OH)_n(OH_2)_m \Leftrightarrow [M^{n+}(OH)_{n-1}(OH_2)_{m+1}]^+ \end{aligned}$$

The acidity or basicity of the metal hydroxide depends on the polarization of the water molecules or hydroxide ions which, in turn, depends on the charge and radius of the metal ion.

The contribution of the acid-base interactions in the surface free energy of the zirconia ceramics and their constituents results probably from the presence of the OH groups on their surface. At the experimental conditions the coordinatively bound and adsorbed water molecules have been removed. However, it is difficult to remove chemically bound water at 110 °C. Of course, the chemistry of the OH groups on the surface of metal oxide depends on the kind of metal and therefore, probably, the highest value of the acid-base component of surface free energy of magnesium oxide is observed (Table III). Also the presence of MgO in the zirconia ceramic system increases the electron-donor parameter of the acid-base component of its surface free energy (Table III).

It is interesting that the contribution of the acid-base interactions in the surface free energy of yttrium oxide is a little higher than in the surface free energy of zirconium oxide, but the presence of yttrium oxide in the zirconia ceramic system, with exception of zirconia ceramic stabilized with 3% yttria, decreases the value of γ_S^{AB}. At present, it is difficult to explain such kind of dependencies. Therefore, further studies should be done to understand this phenomenon.

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