JOURNAL OF
Materials
Communication
CHEMISTRY

Modification of surface properties of alumina by plasma treatment

Gilberto J. Pereira, Maria Lucia P. da Silva, Ing H. Tan and Douglas Gouvea*

Escola Politecnica da Universidade de São Paulo, Depto. de Eng. Metalurgica e de Materiais, Av. Prof. Mello Moraes, 2463 CEP 05508-900, São Paulo, S.P., Brasil

Received 16th November 1999, Accepted 1st December 1999

Tetraethylorthosilicate (TEOS), hexamethyldisilazane (HMDS) and *n*-hexane, plasma deposited on alumina pellets, result in hydrophobic and chemically resistant films, while TEOS treated alumina powder showed significant changes in the zeta potential as a function of pH.

Applications using ceramic powders in technological processes and in industry have increased significantly in recent years. However, mixtures of ceramic powders require that both powders have similar dispersion properties and thus, similar surface properties are important in order to obtain a homogeneous mixture.

Cold plasma processing is a well known and widely used technique for surface modification by etching, corrosion or deposition.[1,2] Plasmas create extremely reactive species such as ions, free radicals and metastable species, which allow reactions to occur at much lower temperatures than in conventional methods, and even reactions unique to plasma conditions. Low quantities of reagents are used and disposed in plasma processing owing to the short treatment times and low pressures, and low energies are used in most processes making them economically attractive.

Organic silicon compounds are widely used in electronic plasma processes owing to their low toxicity and volatility, and the possibility of conformal deposition (*i.e.* deposition which follows strictly the topography of the substrate). Tetraethylorthosilicate (TEOS) is the most common organic silicon compound in use. Pyrolysis of TEOS, which has been studied since the 1960s,[3] can occur at atmospheric or low pressures[4] but requires plasma assisted deposition to occur at low temperatures.[5] Although less used than TEOS, hexamethyldisilazane (HMDS) presents interesting characteristics owing to the presence of Si–C bonds creating the possibility of forming a silicone type structure and the presence of CH_3 groups, which can make surfaces hydrophobic. HMDS had been used for the deposition of SiC : H,[6] for the production of Si/C/N composites in powder form.[7–9] The adsorption of both compounds on alumina[10] can occur through OH groups present in the alumina and the chemisorption is independent of the organic radical present on the silicon molecule.

It has been shown that cellulose surfaces can be made hydrophobic by plasma deposition of HMDS and TEOS.[11] *n*-Hexane could also be used as a cheaper alternative.

Although some work on surface plasma treatment has been done on ceramic surfaces for adhesion improvement in composites,[12,13] to the best of our knowledge, no plasma modification technique has been performed to date to modify the surface hydrophobicity of ceramic materials (powders or sintered samples). The aim of this work was to verify the possible surface changes in sintered alumina pellets and powders by plasma deposition of organic silicon compounds (TEOS, HMDS) as well as *n*-hexane. Alumina was the ceramic material chosen, owing to its low cost and wide applicability. Preliminary investigations were made on the changes of surface properties of alumina powder treated with TEOS. The zeta potential (ζ) as a function of pH was measured to show the modifications of the powder surface acid/base characteristics by determination of the isoelectric point (IEP).

The equipment used for plasma depositions was a parallel plate capacitively coupled reactor powered by a 40 kHz source. The reactor has two 20 cm diameter stainless steel electrodes, 3 cm apart, with one of them being grounded and used as the substrate holder. Monomers were injected *via* a pressure gradient at room temperature, with the working pressure controlled by the pumping speed. For comparison two treatment conditions employed high density plasmas in an inductively coupled reactor (ICP, Table 1).

TEOS, HMDS and *n*-hexane were typically deposited at 0.1–1 Torr, 30–150 W and 2–6 min. Alumina A1000SG (Alcoa) pellets were prepared by pressing at 98 MPa and sintering at 1500 °C for 4 h.

Contact angle measurements were made using a goniometer. Ethanol, propan-2-ol, acetone, tetrachloromethane and *n*-hexane were the liquids chosen to test the effect of solvent polarity on compatibility. Aqueous ammonia, sodium hydroxide, distilled water, sulfuric acid and hydrochloric acid solutions (pH 9, 14, 5, 4 and 1, respectively) were chosen to study the effect of acid/base interactions. The films were then visualised using an optical microscope, to verify any variation on the surface. The adhesion of the films to the substrate was tested by dipping the treated pellet in solutions of sodium hydroxide and sulfuric acid. The thermal behaviour of the films were investigated by heating them to 1000 °C for 15 min and measuring the contact angles.

The deposition conditions used for HMDS, TEOS and *n*-hexane, and the contact angles measured for various liquids are listed in Table 1. All organic solvents (not shown in Table 1) wetted the treated surfaces under all conditions, indicating compatibility with the organic silicon films, independent of polarity. For all treatments hydrochloric acid had the lowest contact angles showing that the films deposited have acidic character. All depositions led to the alumina surface becoming hydrophobic. Untreated alumina pellets are wetted by all solvents probably owing to surface roughness.

Table 2 shows the contact angles measured after heating pellets to 1000 °C for 15 min. The organic part of the deposited film is ablated upon heating, so that heated HMDS films should give Si/C/N type structures, TEOS films should lead to SiO_2 films while *n*-hexane should be completely ablated, resulting in regeneration of an alumina surface. As in films before heating, all organic solvents wetted the surfaces completely probably because the deposited films are porous. For both TEOS and HMDS films, carbon based radicals are expected to be removed by heating whilst for *n*-hexane the film should have been completely removed and the alumina surface behaviour restored. Heated TEOS films are wetted by all non-acidic solvents showing the acidic nature of SiO_2 as expected. A smaller contact angle at higher power for such films means that, since less carbon based radicals are deposited, the heated film has less impurities in its structure. The differently prepared HMDS films differ mainly in thickness, so that heating for 15 min is probably insufficient to change the characteristics of the thicker film deposited at 500 mTorr. However, smaller

Table 1 Contact angles and deposition conditions

			Contact angle/°				
Reagent	Deposition conditions		NaOH	NH_3(aq)	H_2O	H_2SO_4	HCl
HMDS	300 mTorr (ICP)	75 W, 10 min	94	103	103	92	Wetted
		200 W, 4 min	99	103	105	92	Wetted
	100 mTorr	40 W, 2 min	103	107	107	104	70
		100 W, 2 min	103	100	110	98	60
	500 mTorr	40 W, 2 min	97	91	94	105	65
		100 W, 3 min	96	89	96	88	63
TEOS	500 mTorr	30 W, 6 min	91	90	80	92	75
		100 W, 6 min	86	91	74	111	87
		150 W, 6 min	91	95	88	91	75
n-Hexane	1 Torr	50 W, 6 min	100	107	103	103	89
		150 W, 6 min	103	102	95	108	95

Table 2 Contact angles and deposition conditions

		Wetting angle/°				
Reagent	Deposition conditions	H_2O	HCl	H_2SO_4	NH_3(aq)	NaOH
HMDS	100 mTorr, 100 W, 2 min	Wetted	Wetted	6	Wetted	Wetted
	500 mTorr, 100 W, 3 min	38	50	45	43	Wetted
TEOS	500 mTorr, 30 W, 6 min	Wetted	48	57	Wetted	Wetted
	500 mTorr, 150 W, 6 min	Wetted	47	20	Wetted	Wetted
n-Hexane	1 Torr, 150 W, 6 min	Wetted	Wetted	Wetted	Wetted	Wetted

contact angles than for films obtained before heating indicate partial decomposition. This is an interesting characteristic since it shows the versatility of this type of film.

Visualisation by optical microscopy showed no apparent changes in the treated surfaces upon application of organic or inorganic solvent, except for acetone which appears to remove the films. The same behaviour was also observed after thermal treatment and is of interest since it shows that the films are not etched even under severe conditions.

TEOS and HMDS films before and after thermal treatment were dipped for *ca.* 10 min in H_2SO_4 (pH 3) and NaOH (pH 13.2). The films remained adhered to the substrate as shown by optical microscopy and the water contact angles (Table 3). As deposited films did not show any significant difference in hydrophobicity after acid and basic treatment, while significant changes were observed in the thermally treated films. Increases in the contact angles indicate that secondary chemical reactions probably occur, since peeling of the films would not explain the increase in hydrophobicity. Changes in contact angle were more marked for films dipped in H_2SO_4, a strong oxidant, which indicates partial oxidation of carbon based radicals still present after heating. Another possible explanation would be that only the external layers of the films were thermally oxidised and removed by the strong acid leaving a surface covered with organic radicals.

To test dispersion characteristics, alumina powder was treated four times with TEOS deposited at 500 mTorr and 50 W for 6 min, stirring the powder after each treatment. The treated alumina powder was investigated attempting to disperse it in water which did not occur, as expected, since the treated surface is hydrophobic. Addition of propan-2-ol to water to give a 1 : 1 v/v mixture allowed the wetting of the powder and its dispersion. The zeta potential was measured in a solution of absolute ethanol titrating with 2 M HNO_3, using a ESA 8000 MATEC zetameter. Fig. 1 shows the zeta potential measured as a function of pH, for alumina powder treated with TEOS in a solution of absolute ethanol titrated with 2 M HNO_3. A significant variation in the ζ behaviour as a function of pH as well as a significantly different IEP from alumina can be seen. The pH values presented are as measured with no corrections for H activity made.

In summary, we have demonstrated that plasma treatment of ceramic materials is a versatile technique, which can permit surface modification of ceramic powders with different characteristics which should aid in compatibilization for the preparation of homogeneous dispersions.

Acid/base properties of the surfaces could be tailored by careful choice of reagents and post-treatment. For TEOS

Table 3 Water contact angles after dipping in acid and base

	Wetting angle/°	
Reagent and deposition conditions	NaOH, 5 min	H_2SO_4, 15 min
HMDS, 500 mTorr, 100 W, 3 min	84	90
TEOS, 500 mTorr, 150 W, 6 min	90	111
HMDS, same conditions after heating	54	—
TEOS, same conditions after heating	—	60

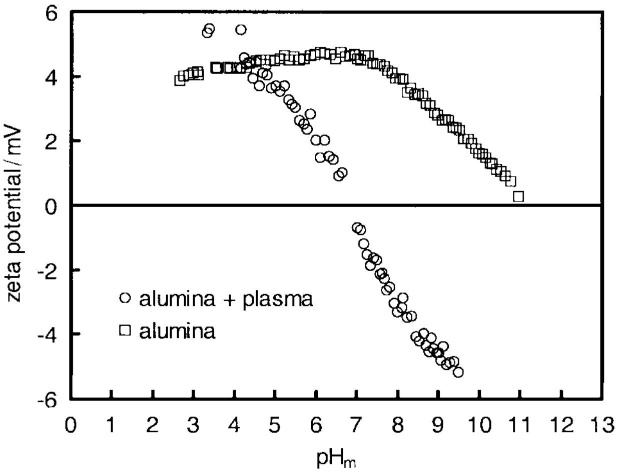

Fig. 1 Zeta potential as a function of pH for untreated and TEOS treated alumina powder. The solvent used was absolute ethanol titrated with 2 M HNO_3. The pH values are measured values and no corrections for H activity were made.

deposition, the power is a fundamental parameter since it controls the amount of carbon in the film, which decreases with power used, and consequently the contact angle is also decreased. On the other hand, for HMDS, the thickness of the film is essential in determining the degree of hydrophobicity after thermal treatment, adding another variable parameter for property modifications. A more detailed study using a variety of reagents and deposition conditions on alumina powder is under way in a specially built plasma reactor equipped with a rotating sample holder.

Notes and references

1 *Plasma Deposition, Treatment and Etching of Polymers*, ed. R. d'Agostino, Academic Press Inc., Boston, MA, 1990.

2 F. Denes, *Elsevier Trends J.*, 1997, TRIP, **5**, no. 1, 23.

3 E. L. Jordan, *J. Electrochem. Soc.*, 1961, **108**, 478.

4 J. Oroshinik and J. Kraitchman, *J. Electrochem. Soc.*, 1969, **115**, 649.

5 H. W. Fry, *Solid State Technol.*, 1994, 31st Mar.

6 M. T. Kim and J. Lee, *Thin Solid Films*, 1997, **303**, 173.

7 S. Y. Park, N. J. Kim, L. I. Hong and H. Lasabe, *Pollimo*, 1992, **16**, 94.

8 J. Weichart and J. Mueller, *Surf. Coat. Technol.*, 1993, **59**, 342.

9 F. Fracassi, R. d'Agostino and P. Favia, *Polym. Prepr.*, 1993, 673.

10 J. P. Alexandex, A. N. Gent and P. N. Henriksen, *J. Chem. Phys.*, 1985, **83**, 5981.

11 I. H. Tan, N. Demarquette, M. L. da Silva, F. T. Degasperi and R. Dallacqua, *Proc. 14th Int. Conf. Plasma Chemistry*, Prague, Czech Republic, August 1999, vol. III, p. 1393.

12 B. Das, *J. Adhes. Sci. Technol.*, 1996, **10**, 1371.

13 G. Akovali and I. Ulkem, *Polymer*, 1999, **40**, 7417.

Communication a909049e