Available online at www.sciencedirect.com
ScienceDirect
Ceramics International 37 (2011) 2015–2019
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

Short communication

Investigation on rheological behavior of 8 mol% yttria stabilized zirconia (8YSZ) powder using Tiron

Shahab Moghadas, Amir Maghsoudipour *, Masoud Alizadeh, Touradj Ebadzadeh

Materials and Energy Research Centre, P.O. Box 31787-316, karaj, Iran

Received 29 September 2010; received in revised form 25 October 2010; accepted 11 January 2011
Available online 18 February 2011

Abstract

In this research, 8 mol% yttria stabilized zirconia (8YSZ) powder were dispersed in de-ionized water by the use of different amounts of Tiron as dispersant. The results of rheological and sedimentation measurements of each suspension were evaluated and the optimum amount of Tiron was selected (0.8% Tiron). Also, various pH were investigated and the best stabilized suspension is achieved at pH 10. Furthermore, the zeta potential of suspension with and without adding dispersant was obtained. The isoelectric point (IEP) of as-received 8YSZ powder was about 8.5 and shifted obviously to acidic region after adding dispersant to the suspension.

Keywords: 8YSZ; Tiron; Rheology; Zeta-potential

1. Introduction

Dispersion of colloidal particles is an important issue in many industries including paints, pigments, pharmaceutical, cosmetics, and ceramics processing for many processes like slip casting, tape casting, dip coating, injection molding, etc. Dispersion is achieved by addition of certain dispersants which are absorbed onto the particles thereby increasing the interparticle forces to overcome aggregation [1–4]. Many variables such as pH, type of dispersant, impurities, solvent, ionic strength, etc. can affect the surface chemistry of particles [5,6].

Zirconia (ZrO_2) is an extremely versatile ceramic that has found use in oxygen pumps and sensors, fuel cells, thermal barrier coatings, and other high-temperature applications, all of which make use of the electrical, thermal, and mechanical properties of this material. Pure zirconia owing to poor ionic conductivity and phase transformation cannot use as a good material for aforesaid applications. Doping of zirconia with a small amounts (3–10 mol%) of a divalent and trivalent oxide can stabilize the cubic fluorite phase, increases oxygen vacancy concentration and therefore enhanced ionic conductivity. The most commonly used dopant is yttria [7,8].

Tiron (4-5-dihydroxy-1,3-benzenedisulfonic acid disodium salt ($C_6H_4Na_2O_8S_2$)) is a dispersant that causes electrostatic repulsion leading to stabilized suspension. Various dispersants have been used to prepare stabilized zirconia suspension in previous researches such as Aluminon [9], polymethacrylic acid (Darven C), diammonium citrate (DAC) and polyethyleneimine (PEI) [6], Triton-X114 [10], MFO and PE [7], NH_4PAA and NH_4PMAA [11], Dolapix CE 64 [1], PSS [12], APMA [13], etc. in aqueous media and some different dispersants [2] such as polyesther-phosphate (PE-312) [4] and fish oil [14] in organic media.

In this study, the effect of Tiron as a dispersant on zeta-potential, sedimentation, and rheological properties of 8YSZ suspensions was investigated.

2. Materials and methods

2.1. Materials

Yttria-stabilized zirconia (8 mol% yttria cubic zirconia (TZ-8Y)) purchased from TOSOH Company (Japan) were used as starting materials for preparation suspensions. The surface area of this powder was $16 \pm 3\ m^2\ g^{-1}$ and granular. Tiron was used as a dispersant (available from FLUKA chemical, UK).

* Corresponding author. Tel.: +98 9123431075; fax: +98 2616201888.
E-mail address: a_maghsoudipour@yahoo.com (A. Maghsoudipour).

0272-8842/$36.00 © 2011 Published by Elsevier Ltd and Techna Group S.r.l.
doi:10.1016/j.ceramint.2011.01.020

Table 1
Suspension formulations.

No.	Vol.%	Solid content (g)	Water (cm^3)	Dispersant (g)	pH
1	5%	9	30	0	10
2	5%	9	30	0.2% = 0.018 (g)	10
3	5%	9	30	0.4% = 0.036 (g)	10
4	5%	9	30	0.6% = 0.054 (g)	10
5	5%	9	30	0.8% = 0.072 (g)	10
6	5%	9	30	1% = 0.09 (g)	10
7	5%	9	30	0.8% = 0.072 (g)	8
8	5%	9	30	0.8% = 0.072 (g)	9
9	5%	9	30	0.8% = 0.072(g)	10
10	5%	9	30	0.8% = 0.072 (g)	11

2.2. Preparation of suspensions

Different slurries were prepared according to Table 1. A flow chart of the preparation process for suspensions is shown in Fig. 1.

KOH solution was employed to adjust the pH values.

2.3. Rheological experiments

The prepared Zirconia suspensions were aged overnight. The rheological properties of the zirconia suspensions were measured by Physica MCR 300 rheometer (produced by Auton Pear). All rheological measurements were conducted at 25 °C and constant volume of suspension (27 cm^3). The effect of different amounts of Tiron on shear rate and shear stress was carried out in the range of 0.1–1000 s^{-1}.

2.4. Zeta-potential measurements

Zeta potential of suspensions were measured by Zetasizer 3000HS (Malvern Co.) at 25 °C.

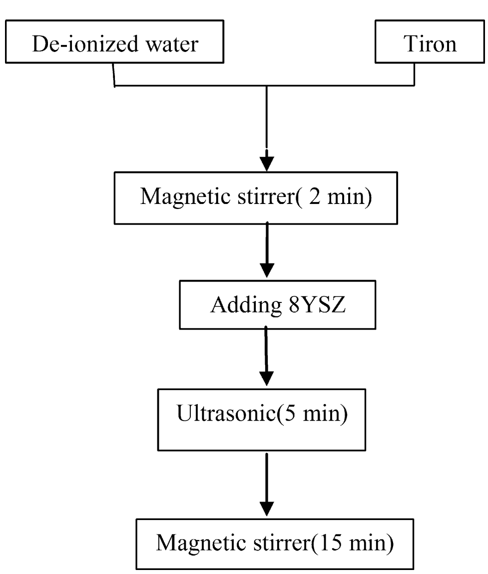

Fig. 1. Flow chart of the preparation process for suspensions.

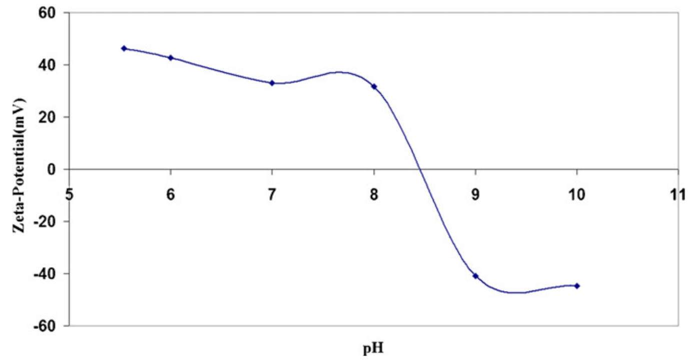

Fig. 2. Zeta-potential versus pH in pure 8YSZ.

2.5. Sedimentation measurements

Some tubes with same height and radius were selected for sedimentation measurements. Suspensions with various amount of powder and dispersant were conditioned 24 h for aging and poured into tubes up to 66 mm height. After 1, 3 and 6 days, the height of non-sediments was measured.

3. Results and discussions

3.1. Zeta-potential measurements

The oxide particles dispersed in water can absorb water molecules and hydration layer forms around the particles. The charged mechanism occurring in various pH ranges follows Eq. (1):

$$MOH_2^+\ (\text{surface}) \xleftarrow{H^+} MOH\ (\text{surface}) \xrightarrow{OH^-} MO^-\ (\text{surface}) + H_2O \qquad (1)$$

where M is metal ions. From Eq. (1) the surface charge of particles depends on the concentration of H^+ and OH^- ions [3,6]. The zeta-potential of the 8YSZ in the absence and presence of Tiron is shown in Figs. 2 and 3, respectively.

The isoelectric point (IEP) of pure 8YSZ (without dispersant) locates at about pH 8.5 that is close to IEP which reported for 3Y-TZP [15]. Pure 8YSZ is positively charged

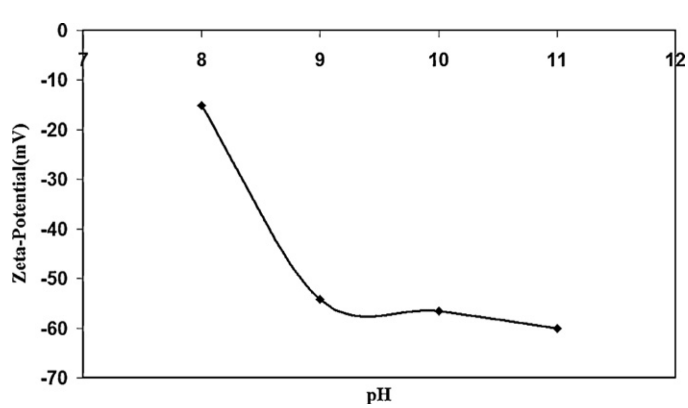

Fig. 3. Zeta-potential versus pH in pure 8YSZ + 0.8% Tiron.

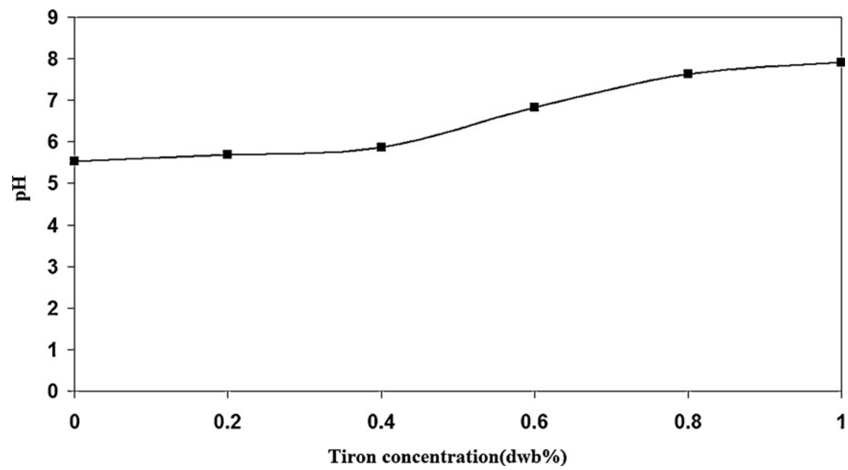

Fig. 4. The variation of pH versus Tiron concentration with adding 8YSZ as-received powder.

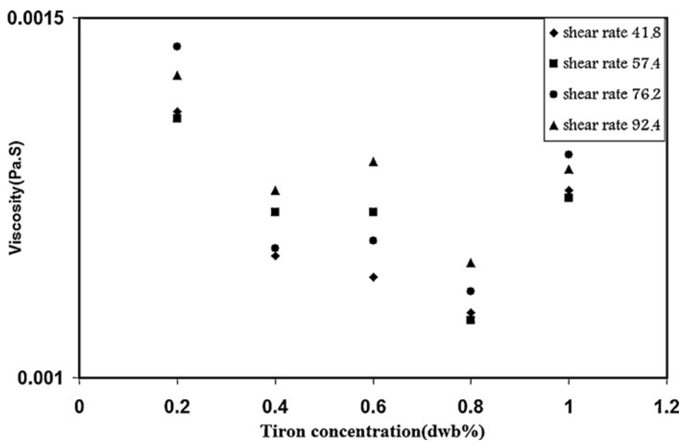

Fig. 5. Viscosity-concentration of Tiron in various shear rates.

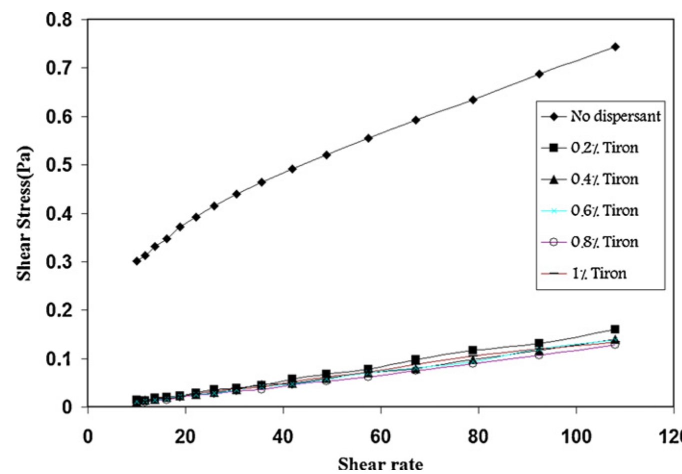

Fig. 6. Shear stress–shear rate (0.1–100 s^{-1}) curves of various Tiron percentages (pH 10).

below IEP and negatively charged above it. Comparison between Figs. 2 and 3 reveals that the IEP of 8YSZ particles is shifted to acid region using 0.8% Tiron. This is because of the negatively charged particles of functional groups of tend to adsorbing onto positively charged 8YSZ particle surfaces while these particles are positively charged at pH lower than IEP [3,5,9,16]. In acidic pH, zeta-potential decreases to IEP because of the positive surface charge and less dissociation of functional groups of Tiron. In basic pH, functional groups of Tiron dissociate completely and absorb on negatively charged zirconia surfaces cause the increase of zeta-potential and improve stability of the suspension [17,18]. Adding Tiron to as-received 8YSZ powder causes the increase of pH values as shown in Fig. 4. By increasing the dispersant percentage, the more dissociation of negative functional groups of dispersant occurs and the positively charged of 8YSZ surfaces liberate more OH^- ions in the suspension.

Suspensions in this research were prepared in alkaline region because yttria is highly basic in this region (IEP is about 11.2). Therefore, liberated yttrium cations act as opposite ions decreasing the double layer [19].

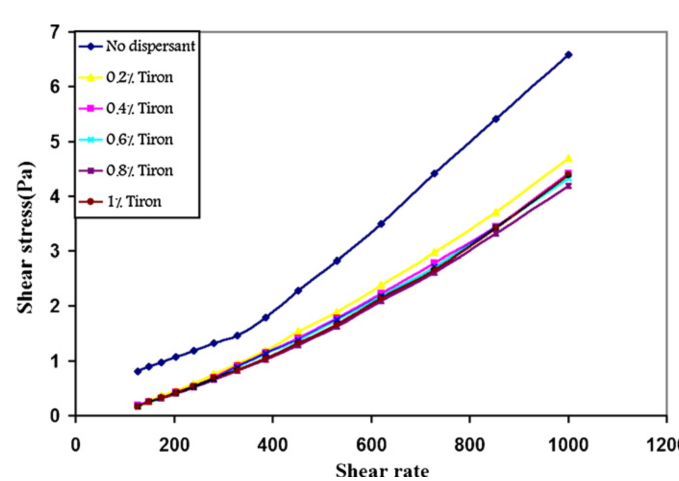

Fig. 7. Shear stress–shear rate (100–1000 s^{-1}) curves of various Tiron percentages (pH 10).

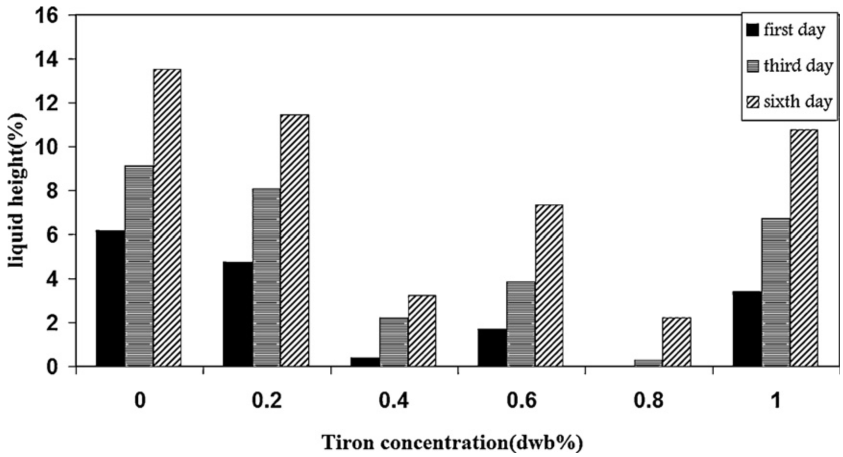

Fig. 8. Sedimentation tests of various percentage of Tiron.

3.2. *Effect of Tiron on the rheological and sedimentation behavior of suspensions*

The pH of suspension was measured after the addition of Tiron in various percentages (Fig. 4). The pH of different suspensions was adjusted to 10 using KOH (1 mol/l) and reported in Table 1.

Fig. 5 shows the changes of viscosity with Tiron concentration at different shear rates. As shown the lowest viscosity occurs after adding 0.8 wt.% Tiron which is adequate for preparation of suspensions at pH = 10. At lower amount of Tiron (lower than 0.8 wt.%), repulsion forces is not affected due to the decrease of absorbing of dispersant and electrical charges on 8YSZ particles surfaces. Above the optimum point (0.8 wt.% Tiron), the remained dispersant that is not absorbed on the particles surface entered into the liquid and acted as an electrolyte which increases the ionic strength. The increased ionic strength, compresses the thickness of double layer and as DLVO theory, confirms electrostatic repulsion energy decreases and agglomeration occurs [20]. Increasing in viscosity after optimum dispersant (0.8 wt.% Tiron) can be due to interaction between dispersant–dispersant and dispersant–solvent [2].

Figs. 6 and 7 show that shear stress–shear rate curves of suspensions containing various Tiron percentages at pH = 10. A completely deflocculated suspension has almost Newtonian behavior but a flocculated suspension shows pseudoplastic behavior in shear stress–shear rate curves [20]. The suspensions without dispersant shows pseudoplastic behavior in low shear rates (0.1–100 s^{-1}) and dilatancy behavior in high shear rates (100–1000 s^{-1}).

Fig. 8 represents the sedimentation test results which are in agreement with other obtained results (Figs. 5–7). The lowest height of liquid (sedimentation) in suspension was obtained with adding 0.8 wt.% Tiron. In suspension with 1% Tiron due to foresaid reasons (such as increasing in ionic strength) agglomeration occurs and the height of liquid in suspension increases.

3.3. *Effect of pH on the rheological and sedimentation behavior of suspensions*

By using the optimum of dispersant (0.8% Tiron), 4 suspensions with different pH were prepared (suspension nos.7–10). The viscosity as a function of pH is shown in Fig. 9. As observed, suspension with 0.8 wt.% Tiron has the lowest viscosity at pH 10. By the increase of pH and due to adding more KOH solution for adjusting pH, ionic strength increases and double electrical layer decreases and therefore agglomeration occurs [6].

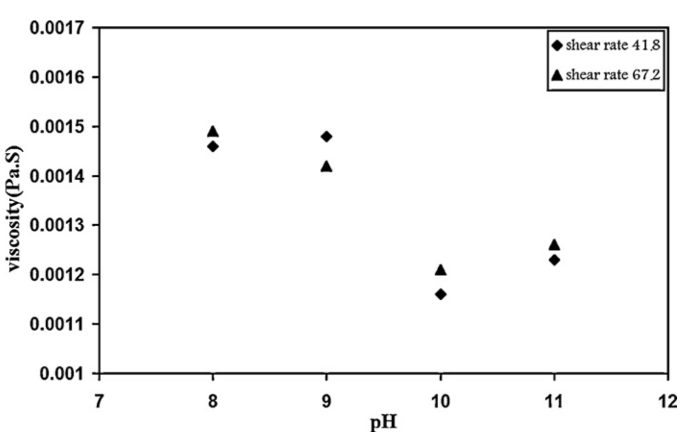

Fig. 9. Viscosity as a function of pH (0.8% Tiron).

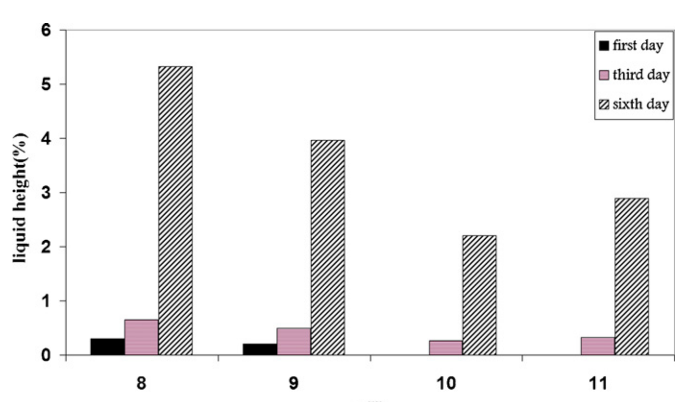

Fig. 10. Sedimentation tests as a function of pH (0.8% Tiron).

The result of sedimentation tests is shown in Fig. 10. In pH 8 and 9, because of low surface charge, zeta-potential (Fig. 3) and dissociation of functional groups of Tiron flocculated has occurred.

4. Conclusions

The zirconia TZ-8Y suspensions stabilized using Tiron that acted as electrostatic repulsion between particles (DLVO theory). All stabilizing suspensions were made in pH 10. This pH obtained with comparison of pH 8, 9, 10 and 11. The results of rheological and sedimentation tests show that the optimum of dispersant percentage was 0.8 wt.% Tiron. By utilizing zeta-potential as a function of pH, pH_{IEP} recognized in the absence and presence of dispersant.

References

[1] S. Prakash, S. Tripathy, M. Raichur, Colloids Surf. A 302 (2007) 553–558.
[2] S. Zurcher, T. Graule, J. Euro. Ceram. Soc. 25 (2005) 863–873.
[3] Y.H. Wang, X.Q. Liu, G.Y. Meng, Ceram. Int. 33 (6) (2007) 1025–1031.
[4] P. Lenormand, D. Caravaca, C. Liberty-Robert, F. Ansart, J. Euro. Ceram. Soc. 25 (2005) 2643–2646.
[5] R.G. Horn, J. Am. Ceram. Soc. 73 (5) (1990) 1117–1135.
[6] T. Fengqiu, H. Xiaoxian, Z. Yufeng, G. Jingkun, Ceram. Int. 26 (2000) 93–97.
[7] A. Mukherjee, B. Maiti, A.D. sharma, R.N. Basu, H.S. Maiti, Ceram. Int. 27 (2001) 731–739.
[8] J.F. Shackelford, R.H. Doremus, Ceramic and Glass Materials: Structure, Properties and Processing, Springer, 2008.
[9] B.J. Briscoe, A.U. Khan, P.F. Luckham, J. Euro. Ceram. Soc. 18 (1998) 2169–2173.
[10] J. Zhang, F. Ye, J. Sun, D. Jiang, M. Iwasa, Colloids Surf. A: Physciochem. Eng. Aspects 254 (2005) 199–205.
[11] G. Wang, L. Gao, Ceram. Int. 26 (2000) 187–191.
[12] B. Jachimska, Z. Adamczyk, J. Euro. Ceram. Soc. 27 (2007) 2209–2215.
[13] L. Saravanan, S. Subramanian, Colloids Surf. A 252 (2005) 175–185.
[14] S.D. Kim, S.H. Hyun, J. Moon, J.-H. Kim, R.H. Song, J. Power Sources 139 (2005) 67–72.
[15] Q. Tan, Z. Zhang, Z. Tang, S. Luo, K. Fang, Mater. Chem. Phys. 80 (2003) 615–619.
[16] J.A. Lewis, J. Am. Ceram. Soc. 83 (10) (2000) 2341–2359.
[17] F. Shojai, A.B.A. Pettersson, T.M. Ntylae, J.B. Rosenholm, J. Euro. Ceram. Soc. 20 (2000) 277–283.
[18] Z. Xie, J. Ma, Q. Xu, Y. Huang, Y.B. Cheng, Ceram. Int. 30 (2004) 219–224.
[19] J.C. Farinas, R. Moreno, J. Requena, J.S. Moya, Mater. Sci. Eng. A 109 (1989) 97–99.
[20] A.K. Nikumbh, H. Schmidt, K. Martin, F. Porz, J. Mater. Sci. 26 (1991) 3649–3656.