

## Production of submicron sized boric acid particles by wet milling\*

Mehmet İkbal IŞIK, Emine BAKAN, Özgenur KAHVECİOĞLU, Servet TİMUR  
*Metallurgical & Materials Engineering Department, Chemical and Metallurgical Faculty,  
İstanbul Technical University, Ayazağa Campus, 34469, İstanbul-TURKEY  
e-mail: mehmet.isik@itu.edu.tr*

Received 10.05.2010

### Abstract

Submicron sized boric acid particles are used in traditional lubrication oils as they provide a low friction coefficient and they are friendly to the environment. In the present study, size and structure changes in high energy ball wet milled boric acid particles were investigated and characterized by X-ray diffraction (XRD), BET, and thermo-gravimetric/differential thermal analysis (TG-DTA). It was seen that increasing time of milling resulted in smaller particle formation and a larger specific surface area. Moreover, it appeared that thermal decomposition temperatures were not size dependent.

**Key Words:** Boric acid, nanoparticle, wet milling, boron compound, ultrafine powder

### Introduction

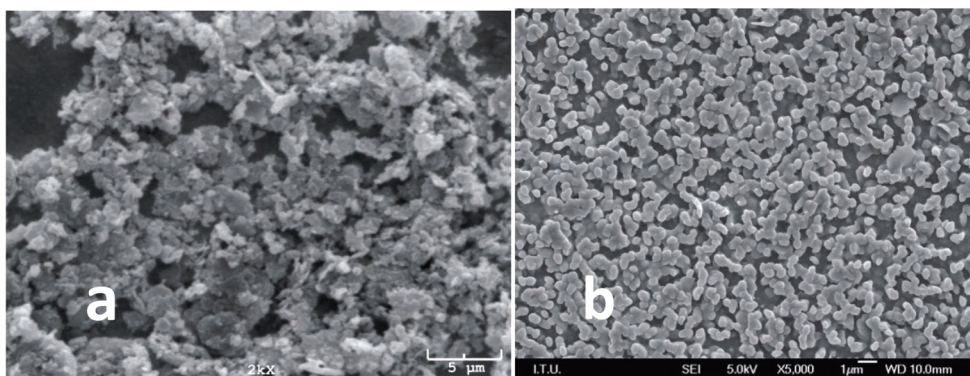
Boric acid ( $H_3BO_3$ ) has always been a very important material due to its broad range of applications such as in medicine (Barranco and Eckhert, 2004; Prentice et al., 2006), cosmetics (Fail et al., 1998), the automotive industry (Erdemir, 2000), metallurgy (Mergen, 2003; Jung et al., 2005), and also for miscellaneous purposes in other areas (Hu et al., 2009; Ohishi et al., 2009).

Erdemir et al. (1990) showed that friction between automobile engine parts could be greatly reduced using microscopic particles of boric acid.

Several techniques are available for producing submicron particles such as Sol-Gel (Suciu et al., 2006), microwave plasma chemical vapor deposition (Liu et al., 1999), vapor phase synthesis (Moravec et al., 2007), wet chemical (Mergen et al., 2003), pyrolysis (Brankovic et al., 2005), hydrolysis (Patel et al., 2008), and milling (Dabhade, 2007).

Dry milling and flame spray synthesis of boric acid particles were investigated within our research group in previous studies (Işık, 2007). Figure 1a shows 120 min dry milled and Figure 1b shows flame spray synthesized boric acid particles' SEM images.

\*Paper presented at the 6th Nanoscience and Nanotechnology Conference (NanoTRVI), İzmir, Turkey, June 15-18, 2010.



**Figure 1.** SEM image of boric acid particles produced by different techniques; (a) 120 min dry milled and (b) flame spray synthesized.

In this study wet milling was investigated for production of submicron boric acid particles. Size and structure changes depending on milling duration were investigated systematically.

## Experimental

The precursor material used for high energy ball milling was high purity (>99.5%) boric acid powder. The ball to powder ratio (BPR) was kept constant in all sets of experiments as 10:1. Milling was done with stainless steel balls and containers using 15 mL of hexane as dispersant. Experimental milling durations were chosen as 30, 60, 120, 180, and 240 min. In order to remove moisture the boric acid precursor powder was heated to 85 °C and kept at this temperature for 24 h.

## Results and Discussion

### X-ray diffraction analysis

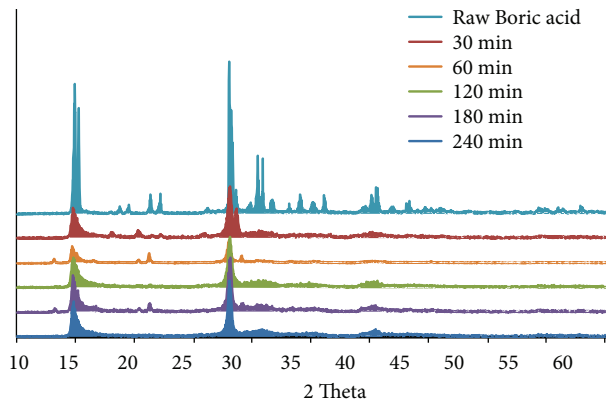
Wet milled boric acid particles were characterized by X-ray diffraction (Figure 2). Since stainless steel ball were used for milling, it is possible to see some impurity peaks, mainly iron, chromium, and nickel. From the shortest to the longest milling times, there were no peaks resulting from any impurities. However, this cannot be interpreted as showing that there were no stainless steel particles penetrating into the powder because of XRD technique limitations.

Figure 2 clearly shows the decrease in peak intensity, which indicates that particle size reduction occurred. Moreover, there is no significant change either in peak intensity or in peak width.

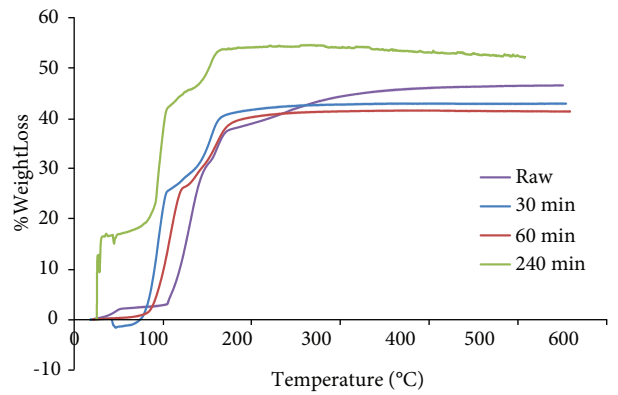
### Thermo-gravimetric/differential thermal analysis

The weight loss versus temperature graph can be seen in Figure 3. It shows that weight loss percentage is decreasing for 30 and 60 min. However, for 240 min milling, there is a great increment in weight percent loss.

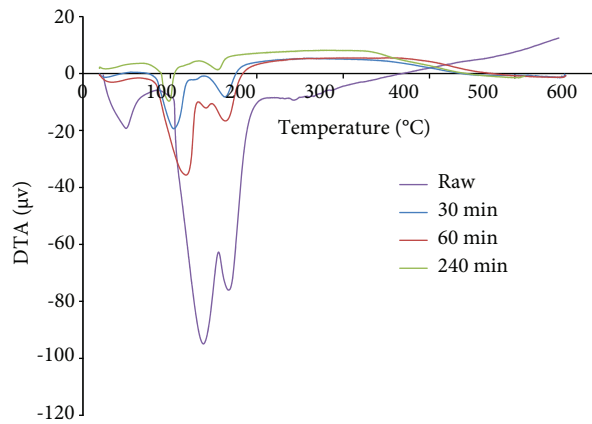
The DTA versus temperature graph of the raw and 30-60-240 min wet milled boric acid particles up to 500 °C can be seen in Figure 4. It shows that there were no shifts in decomposition temperatures. Weight loss percentage is decreasing for 30 and 60 min. However, for 240 min milling, there is a great increment in weight percent loss.



**Figure 2.** X-ray diffraction patterns of the wet milled boric acid particles.



**Figure 3.** Thermo-gravimetric analysis of the wet milled boric acid particles up to 500 °C.



**Figure 4.** DTA of the raw and 30-60-240 min wet milled boric acid particles.

### BET specific surface area analysis

Specific surface area of the powder was analyzed using the BET technique and the results are given in the Table.

**Table.** SSA results of 30 min and 240 min milled particles.

	30 min	240 min
SSA (m <sup>2</sup> /g)	9.28	13.1
Particle diameter (nm)	450	319

Making some assumptions about particle shape and especially assuming that particles are spherical, SSA can be used for particle size calculation according to Eq. (1).

$$SSA = \frac{6}{d\rho} \rho = \text{Density}, d = \text{Diameter of particle} \quad (1)$$

Calculations yielded particle diameters of 450 nm and 319 nm for 30 min and 240 min, respectively. Compared to the dry milling conditions (Işık, 2007) wet milling is capable of producing finer particles on the basis of SSA values.

## Conclusions

Submicron sized boric acid particles have been produced by high energy ball wet milling. Keeping all other parameters constant, 30, 60, 120, 180, and 240 min milling levels were investigated in order to understand size and structure changes depending on time. From XRD analysis, it is understood that there was no widening but only an intensity drop in diffraction patterns. TG and DTA analyses showed that there was a slight change that can be ignored. BET analyses showed that extending milling time created larger specific surface area up to 13.1 m<sup>2</sup>/g. It was also seen that wet milling generated smaller particles than dry milling.

## Acknowledgements

The authors would like to thank Miray Çelikbilek M.Sc., Şeyma Duman M.Sc., and Kübra Yumakgil M.Sc.

## References

- Barranco, W.T. and Eckhert, C.D., "Boric Acid Inhibits Human Prostate Cancer Cell Proliferation", *Cancer Letters*, 216, 21-29, 2004.
- Brankovic, G., Brankovic, Z., Goes, M.S., Paiva-Santos, C.O., Cilense, M., Varela, J.A. and Longo, E., "Barium Strontium Titanate Powders Prepared by Spray Pyrolysis", *Materials Science and Engineering B*, 122, 140-144, 2005.
- Dabhade, V.V., Rama Mohan, T.R. and Ramakrishnan, P., "Nanocrystalline Titanium Powders by High Energy Attrition Milling", *Powder Technology*, 171, 177-183, 2007.
- Erdemir, A., Fenske, G.R. and Erck, R.A., "A Study of the Formation and Self-Lubrication Mechanisms of Boric Acid Films on Boric Oxide Coatings", *Surface and Coatings Technology*, 43-44, 588-596, 1990.
- Erdemir, A., "Lubrication with Boric Acid Additives", US Patent Office, Patent No: 6025306, 2000.
- Fail, P.A., Chapin, R.E., Price, C.J. and Heindel, J.J., "General Reproductive, Developmental, and Endocrine Toxicity of Boronated Compounds", *Reproductive Toxicology*, 12, 1-18, 1998.
- Hu, S., Chen, Y, Zhu, H., Zhu, J., Yan, N. and Chen, X. "In Situ Synthesis of di-n-butyl l-tartrate-Boric Acid Complex Chiral Selector and Its Application in Chiral Microemulsion Electrokinetic Chromatography", *Journal of Chromatography A*, 1216, 7932-7940, 2009.
- Işık, M.İ., Production of Nano-boric Acid by Flame Synthesis", M.Sc. Thesis, İstanbul Technical University, Institute of Science and Technology, 2007.
- Jung, D.S., Hong, S.K., Lee, H.J. and Kang, Y.C., "Effect of Boric Acid Flux on the Characteristics of (Cetb)Mgal11o19 Phosphor Particles Prepared by Spray Pyrolysis", *Journal of Alloys and Compounds*, 398, 309-314, 2005.
- Liu, B., Gu, H. and Chen, Q., "Preparation of Nanosized Mo Powder by Microwave Plasma Chemical Vapor Deposition Method", *Materials Chemistry and Physics*, 59, 204-209, 1999.
- Mergen, A., Demirhan, M.H. and Bilen, M., "Processing of Boric Acid from Borax by a Wet Chemical Method" *Advanced Powder Technol.*, 14, 279-293, 2003.
- Ohishi, K, Itadani, T., Hayashi, T., Nakai, T. and Horii, F., "Role of Boric Acid in the Formation of Poly(Vinyl Alcohol)-Iodine Complexes in Undrawn Films" *Polymer*, In Press, accepted manuscript, 2009.
- Patel, N., Patton, B., Zanchetta, C., Fernandes, R., Guella, G., Kale, A. and Miotello, A., "Pd-C Powder and Thin Film Catalysts for Hydrogen Production by Hydrolysis of Sodium Borohydride", *International Journal of Hydrogen Energy*, 33, 287-292, 2008.
- Prentice, L.H., Tyas, M.J. and Burrow, M.F., "The Effects of Boric Acid and Phosphoric Acid on the Compressive Strength of Glass-Ionomer Cements", *Dental Materials*, 22, 94-97, 2006.
- Suciu, C., Gagea, L., Hoffmann, A.C. and Mocean, M., "Sol-Gel Production of Zirconia Nanoparticles with a Neworganic Precursor", *Chemical Engineering Science*, 61, 7831-7835, 2006.