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Preventing hydrolysis of AlN powders with organophosphate coating in aqueous media

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Abstract: The coating of aluminum nitride powder has a great importance industrially and environmentally. AlN can be rapidly hydrolyzed to aluminum hydroxide and ammonia in the atmosphere or water media. To prevent the hydrolysis of AlN, the inorganic or organic based coatings are used frequently. For the first time, this study describes the phosphate esters as organophosphate coating used for the inhibition of hydrolysis reaction of AlN in its water suspension. Phenyl phosphate showed the best inhibition against AlN hydrolysis with an easy application technique and at low concentration of 0.005 M. AlN coating efficiency was proved by spectroscopic and imaging methods. It was concluded that the coating acquired the protective properties of phenyl phosphate through its water repellence.

Keywords: aluminum nitride; organophosphate; coating; hydrolysis protection.

INTRODUCTION

Aluminum nitride is an industrially important ceramic with its low dielectric coefficient, high electrical resistance and thermal conductivity, and low thermal expansion coefficient.[1] AlN is frequently used ceramic in the production of ceramics and electronic devices as an additive,[2,3] semiconductor,[4] supercapacitors[5] and surface coating.[3] AlN must be utilized under controlled conditions because of its sensitivity to oxidation and hydrolysis in atmosphere.[6] In water, it highly decomposes to aluminum hydroxide and ammonia depending on the temperature and pH.[7]

In AlN production, 700 °C is a critical temperature, and aluminum powder can be reacted by the nitrogen in atmosphere to form AlN.[8] For that, there is a

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high amount of AlN in the dross of aluminum recycling facilities, especially the secondary dross could contain approximately 14 % of AlN in the total quantity.[9] The high reactivity of AlN causes the storage and disposal problems for AlN products and the dross of Al recovery plants. In addition, protecting AlN particles against hydrolysis is critical in preventing ammonia related environmental effects.[10] Hydrolysis of AlN occurs by both mechanisms in several steps in which NH_3 and $Al(OH)_3$ are produced, and the hydrolysis mechanism are related to temperature as shown below.[11] On the other hand, crystalline $Al(OH)_3$ (bayerite) to become more stable phase can form from amorphous AlOOH (boehmite) at room temperature:[11]

$$AlN + 3H_2O \rightarrow Al(OH)_3 + NH_3 \ (T < 351 \text{ K}) \text{ or} \tag{1}$$

$$AlN + 2H_2O \rightarrow AlOOH + NH_3 \ (T > 351 \text{ K}) \tag{2}$$

$$(AlOOH)_{\text{amorphous}} + H_2O \rightarrow Al(OH)_{3,\text{crystalline}} \tag{3}$$

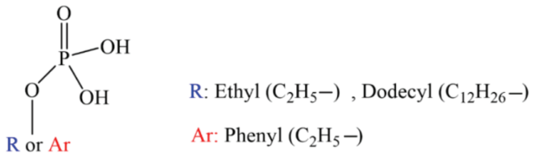
For these reasons, the coating of AlN surface to avoid its decomposition is essential for manufacturing and waste management[12] also the surface modification is a necessity for the deagglomeration and mixing problems of the ceramics production with AlN.[12] Inorganic and organic modifiers can be utilized for coating AlN surface against oxidation and hydrolysis in atmosphere. While phosphoric acid,[13,14] silicate[15] and their derivatives could be used to get water immiscible surface on AlN in the inorganic treatment, the organic molecules with their long chain carboxylic acids, or hydroxyl/amine groups could be utilized to obtain a water repelling surface on AlN such as sebacic acid,[16] citric acid,[17] oleic acid,[18] silicic acid,[19] dodecylamine,[20] cetyl alcohol[20] and stearic acid.[20]

In this study, we investigated to prevent AlN hydrolysis by forming a protective layer on the surface of AlN using organophosphate (OP) molecules such as ethyl phosphate (EP), phenyl phosphate (PP) and dodecyl phosphate (DP) esters. The resistance of treated powders of AlN to hydrolysis was characterized by X-ray diffraction (XRD), fourier transform infrared (FTIR), contact angle, scanning electron microscopy (SEM) techniques and pH measurements. It was observed that the hydrolysis resistance was directly related to the water repellency of the OP used in treatment process of AlN.

EXPERIMENTAL

Materials

AlN powder was purchased by Alfa Aesar (with the particle size under 4 μm). EP, PP and DP (presented in Scheme 1) were obtained from TCI. Ethanol in high purity was purchased from Sigma. The solutions of OP esters were prepared with the appropriate amount of AlN and 30 % ethanol in deionozed water. 0.1 M HCl and NaOH were used to adjust the pH of the solutions. All the experiments were performed at room temperature.



Scheme 1. Chemical structure of OPs.

Apparatus

Mettler Toledo SevenCompact was used for pH measurements in the AlN suspensions. The wettability of the treated AlN samples was performed by SEO Phoenix 300 contact meter with a static water contact angel technique. A Panalytical Empyrean with a CuKα source at a 0.154 nm wavelength (Tokyo, Japan) was used to record XRD spectra. FTIR spectra were obtained using Shimadzu IR-Affinity 1 (Kyoto, Japan). SEM micrographs were obtained with a Jeol 6390 LV SEM operated at 10 kV after gold coating by a sputter coater.

Methods

pH responses of AlN suspensions in the existence of various OP esters were performed at 2 % AlN and 0.025 M of OP ester. The XRD spectra, contact angel measurements, FTIR spectra and SEM micrographs were obtained from the samples filtered and dried at 60 °C in vacuum oven after treating with OP esters and water in the appropriate solutions.

RESULTS AND DISCUSSION

The pH change in a particular hydrolysis condition has an importance since the hydrolysis product, NH_3, of AlN increases the pH of the solution. Because of the effect of OP ester on the hydrolysis of AlN in water, the pH test is useful for monitoring the hydrolysis of AlN *vs*. time. In Fig. 1, the results of pH *vs*. time for the suspensions of various OP ester and AlN were presented. Initial pH of the OP ester solution was adjusted in the range of pH 6–7 to monitor pH accurately before the addition of AlN into the media. The pH monitoring reached maximum value at pH 10, for the suspension of water and AlN, in 1500 min. This result confirmed the NH_3 production after hydrolysis reaction of AlN in water. On the other hand, the addition of OP esters into the media inhibited the hydrolysis reaction completely with a non-significant difference at pH, Fig. 1, with a result similar to the literature.[17,18,20] Since the principle of the chemical coverage of AlN surface against hydrolysis reaction was modifying the surface with organic molecules to increase the hydrophobicity of its surface,[21] it could be said that all three modifiers were suitable to succeed in covering the AlN surface regardless the type of organic group attached to phosphate in OP esters such as EP, PP and DP. On the other hand, Egashira *et al.* proved that the oxide sensitive group binding to AlN as well as the organic group in a modifier molecule is important in preventing hydrolysis by showing lower efficiency of dodecylamine to cethyl alcohol, while dodecyl group has a longer carbon skeleton than cethyl group.[20] After the results shown in Fig. 1, the water contact angle method was needed as a technique to measure surface hydrophobicity of OP ester treated AlN. For this purpose, the surface treated AlN powders obtained in the same conditions from Fig. 1 were filtered and dried at 60 °C in vacuum oven, while the water-treated AlN was obtained by the same way for comparison.

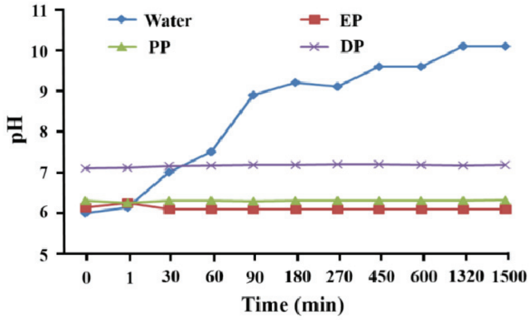


Fig. 1. pH responses *vs*. time for AlN suspensions in water and water/OP esters.

The contact angel measurements in Fig. 2 showed that maximum water repelling was obtained from the samples treated with DP (75.7°) and PP (69.8°), while EP (25.9°) treated sample showed a limited repelling. In addition, the water treated AlN sample in Fig. 2 interestingly gave a higher value, than EP treated sample, namely 42.9°. As expected, non-treated AlN sample in Fig. 2 showed no water repelling because of its reactivity.

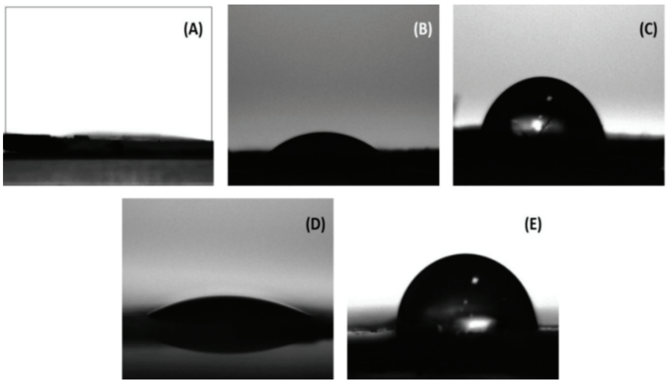


Fig. 2.The water contact angle measurements of non-treated AlN (A), water (B), PP (C), EP (D) and DP treated (E) AlN powders.

FTIR spectra of non-treated and treated AlN samples are presented in Fig. 3. The broad band around 700 cm^{-1} was attributed to the absorption of Al–N vibration.[12] The water treated sample of AlN showed two bands at 696 and 1032 cm^{-1} from the adsorption of Al–O vibrations, at the range of 3443–3650 cm^{-1} of O–H vibrations arisen from water vapor adsorbed on the powder sample. In PP and EP treated AlN samples, there was not a significant adsorption band without the broad band of Al–N vibrations because of low alkyl chain and aromatic group attached to the surface of AlN particle. DP treated AlN showed distinctly aliphatic adsorption bands for C–C and C–H symmetric/ asymmetric vibrations in its long carbon skeleton at 1070, 1144, 1220, 1470, 2847, 2915 and 2961 cm^{-1}.

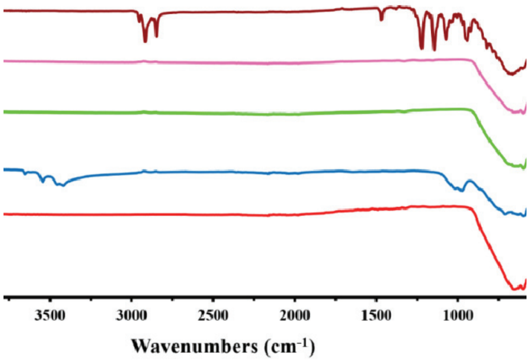


Fig. 3. FTIR spectra of non-treated (A), water treated (B), PP treated (C), EP treated (D) and DP treated (E) AlN samples.

XRD spectra of the samples of treated and non-treated AlN powders are presented in Fig. 4. In Fig. 4, the characteristic peaks of AlN powder at 2θ 33.3, 36.1, 37.9, 49.9, 59.4 and 66.1° corresponding to (100), (002), (101), (102), (110) and (103), respectively (JCPDS card number: 00-001-0287). After water treatment of AlN powders, the appearance of the diffraction peaks at 2θ 18.8, 20.4, 27.9, 40.7 and 53.2° corresponding to (001), (100), (101), (111) and (112), respectively, was resulting from the formation of $Al_2O_3 \cdot 2H_2O$ due to the hydrolysis reaction of AlN in water. From Fig. 4, while it was understood that DP and PP protected AlN well against the hydrolysis reaction, it was concluded that EP did not provide a complete protection against hydrolysis since both the diffraction peaks for AlN and $Al_2O_3 \cdot 2H_2O$ were observed in the diffraction spectrum of EP treated AlN sample.[22] However, it was concluded that PP provided complete protection for AlN against hydrolysis while DP protected only partially, since very weak $Al_2O_3 \cdot 2H_2O$ peaks were observed in AlN sample treated with DP, while $Al_2O_3 \cdot 2H_2O$ peaks were not observed in AlN sample treated with PP. This result showed that the PP treatment provide the best protection for AlN against the hydrolysis reaction in water.

Particle morphologies of AlN powders after treatment with OP esters were critical for the microstructural evolution. The SEM micrographs of AlN samples treated by water and OP esters are presented in Fig. 5. The formation of aluminum oxide was confirmed from the polymorphs of Al–O formation between the adjacent particles for the sample of water treated AlN powder. While there was no significant change in particle morphology for DP and PP treated AlN, a similar degradation was observed in the EP treated AlN sample similar to the water treated AlN sample due to Al-O formation on the sample surface.[6]

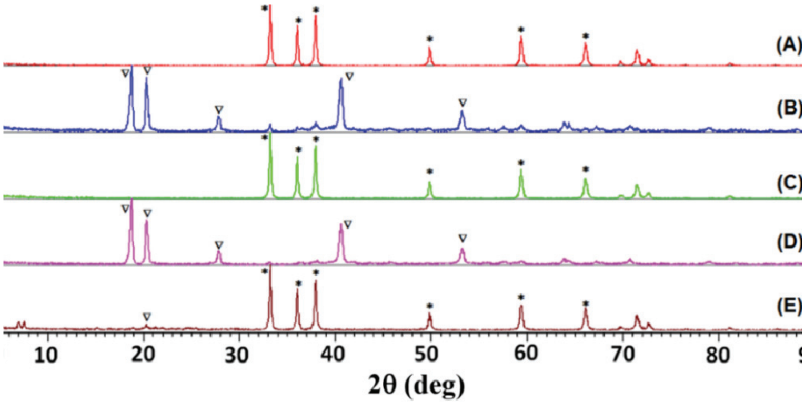


Fig. 4. XRD spectra of non-treated (A), water treated (B), PP treated (C), EP treated (D) and DP treated (E) of AlN samples.

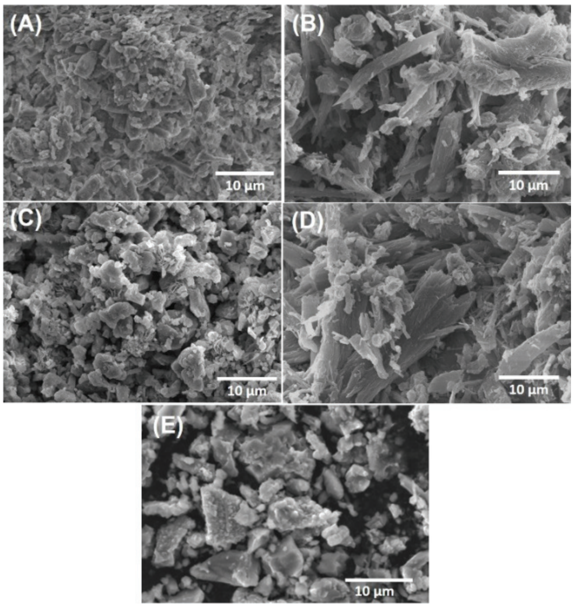


Fig. 5. SEM micrographs of water (A), PP (B), EP (C) and DP treated (D) of AlN samples, and (E) untreated AlN.

After it was concluded that the best protection was obtained as a result of treatment of AlN with PP, in order to examine the effect of PP concentration on AlN protection against the hydrolysis reaction, the pH changes of AlN water suspensions containing PP in different concentrations were monitored and plotted

Fig. 6. From the pH change of 0.0001 M PP treatment of AlN in water in Fig. 6, it was concluded that the AlN samples treated with PP at 0.001 M and higher concentrations protected the AlN powders against the hydrolysis reaction. This result showed that PP could inhibit the hydrolysis reaction of AlN at lower concentrations better than water-repellent and hydrolysis protective materials used for similar purposes in the literature.

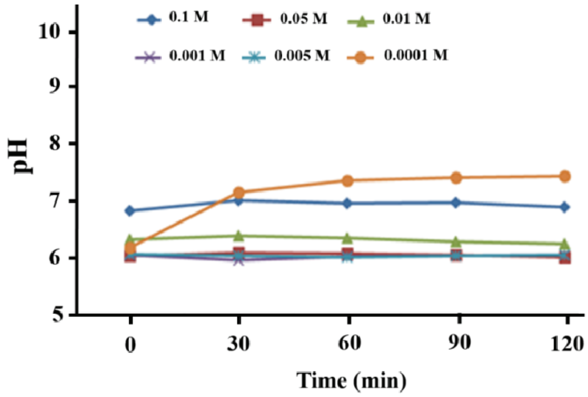


Fig. 6. pH responses *vs*. time for AlN suspensions in water with various PP concentrations.

CONCLUSION

The capability of water repelling and hydrolysis inhibition with the coating of AlN surface are very important in order to avoid the environmental poisoning and the degradation of AlN. The inorganic treatment with mostly phosphate compounds and organic treatment with mostly oxygen functional compounds have been utilized for this purpose. In this paper, alkyl and aryl functional phosphate esters were used for inhibition of hydrolysis reaction first time, and PP as aryl functional coating of AlN powder showed the best performance in very dilute concentration for avoiding hydrolysis and degradation of AlN, so it seems that this type of materials are very useful and promising for coating AlN against hydrolysis reaction with an easy application.

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ИЗВОД

СПРЕЧАВАЊЕ ХИДРОЛИЗЕ ПРАХА AlN ПОМОЋУ ОРГАНОФОСФАТНИХ ПРЕВЛАКА У ВОДЕНОЈ СРЕДИНИ

CEREN KAYA[1], OĞUZ BAYINDIR[1,2], SARUHAN SAKLAR[3], ORHAN ATAKOL[4] и HÜSEYİN ÇELİKKAN[1]

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Облагање прахом алуминијум-нитрида има велики индустријски и еколошки значај. У атмосфери или воденој средини AlN брзо подлеже реакцији хидролизе при чему настају алуминијум-хидроксид и амонијак. Да би се спречила хидролиза AlN, често се користе неоргански или органски премази. Први пут у овом раду описана је примена фосфатних естара као органофосфатних премаза за инхибицију реакције хидролизе AlN у воденој средини. Најбољи резултати инхибиције хидролизе AlN добијени су у случају фенил-фосфата који се користи једноставном техником наношења и при ниској концентрацији од 0,005 M. Ефикасност превлаке AlN је потврђена спектроскопским и *imaging* методама. Закључено је да фенил-фосфат инхибира реакцију хидролизе захваљујући његовој слабој апсорпцији воде.

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REFERENCES

1. L. M. Sheppard, *Am. Ceram. Soc. Bull.* **69** (1990) 1801
2. G. Hu, C. Q. Chen, K. T. Ramesh, J. W. McCauley, *Acta Materialia* **60** (2012) 3480 (https://doi.org/10.1016/j.actamat.2012.03.011)
3. J. L. Qi, L. P. Wang, Y. Zhang, X. Guo, W. Yu, Q. Wang, K. Zhang, P. Ren, M. Wen, *Surf. Coat. Technol.* **405** (2021) 126724 (https://doi.org/10.1016/j.surfcoat.2020.126724)
4. Q. Wang, Y. Lu, S. Mishin, Y. Oshmyansky, D. A. Horsley, *J. Microelectromechanical Syst.* **26** (2017) 1132 (https://doi.org/10.1109/JMEMS.2017.2712101)
5. S. Hao, L. Zhang, X. Wang, G. Zhao, P. Hou, X. Xu, *Energy Fuels* **35** (2021) 12628 (https://doi.org/10.1021/acs.energyfuels.1c01420)
6. J. Li, M. Nakamura, T. Shirai, K. Matsumaru, C. Ishizaki, K. Ishizaki, *J. Am. Ceram. Soc.* **89** (2006) 937 (https://doi.org/10.1111/j.1551-2916.2005.00767.x)
7. A. Kocjan, A. Dakskobler, K. Krnel, T. Kosmač, *J. Eur. Ceram. Soc.* **31** (2011) 815 (https://doi.org/10.1016/j.jeurceramsoc.2010.12.009)
8. G. Long, L. M. Foster, *J. Am. Ceram. Soc.* **42** (1959) 53 (https://doi.org/10.1111/j.1151-2916.1959.tb14066.x)
9. H. Feng, G. Zhang, Q.. Yang, L. Xun, S. Zhen, D. Liu, *Processes* **8** (2020) 1269 (https://doi.org/10.3390/pr8101269)
10. M. Mahinroosta, A. Allahverdi, *J. Environ. Manage.* **223** (2018) 452 (https://doi.org/10.1016/j.jenvman.2018.06.068)
11. S. Fukumoto, T. Hookabe, H. Tsubakino, *J. Materials Sci.* **35** (2000), 2743 (https://doi.org/10.1023/A:1004718329003)
12. M. Oliveira, S. Olhero, J. Rocha, J. M. F. Ferreira, *J. Colloid Interface Sci.* **261** (2003), 456 (https://doi.org/10.1016/S0021-9797(03)00065-1)
13. R. Senthil Kumar, K. Rajeswari, B. Praveen, U. N. S. Hareesh, R. Johnson, *J. Am. Ceram. Soc.* **93** (2010) 429 (https://doi.org/10.1111/j.1551-2916.2009.03418.x)

14. Q. Wang, S. M. Olhero, J. M. F. Ferreira, W. Cui, K. Chen, Z. Xie, R. Riman, *J. Am. Ceram. Soc.* **96** (2013) 1383 (https://doi.org/10.1111/jace.12288)
15. Y. H. Koh, J. J. Choi, H. E. Kim, *J. Am. Ceram. Soc.* **83** (2000) 306 (https://doi.org/10.1111/j.1151-2916.2000.tb01190.x)
16. Y. Shimizu, J. Hatano, T. Hyodo, M. Egashira *J. Am. Ceram. Soc.* **83** (2000) 2793 (https://doi.org/10.1111/j.1151-2916.2000.tb01633.x)
17. S. Wildhack, G. Rixecker, F. Aldinger, *J. Am. Ceram. Soc.* **83** (2005) 2391 (https://doi.org/10.1111/j.1551-2916.2005.00467.x)
18. H. B. Shan, Y. Zhu, Z. T. Zhang, *Br. Ceram. Trans.* **98** (1999) 146 (https://doi.org/10.1179/096797899680363)
19. G. Yu, J. Xie, S. Wang, Y. Wang, T. Wang, L. Fan, L. Zhang, F. Lei, Y. Shi, L. Yu, *Ceram. Int.* **47** (2021) 29253 (https://doi.org/10.1016/j.ceramint.2021.07.089)
20. M. Egashira, Y. Shimizu, S. Takatsuki, *J. Mater. Sci. Lett.* **10** (1991) 994 (https://doi.org/10.1007/BF00721824)
21. A. Kocjan, A. Dakskobler, T. Kosmac, *Int. J. Appl. Ceram. Technol.* **8** (2011) 853 (https://doi.org/10.1111/j.1744-7402.2010.02516.x)
22. R. S. Kumar, U. S. Hareesh, P. Ramavath, R. Johnson, *Ceram. Int.* **37** (2011) 2583 (https://doi.org/10.1016/j.ceramint.2011.04.131).