

WON YOUNG HEO¹, SUNG HWA BAE^{2*}, INJOON SON^{1*}

ENHANCED ENERGETIC PERFORMANCE OF POLYVINYLIDENE FLUORIDE-COATED ZIRCONIUM PARTICLE

In this study, energetic behaviors of polyvinylidene fluoride (PVDF)-coated zirconium (Zr) powders were investigated using thermogravimetric analyzer-differential scanning calorimetry (TGA-DSC). PVDF-coated Zr powder had 1.5 times higher heat flow than ZrO₂-passivated Zr powder. PVDF-coated Zr powder had a Zr-F compound formed on its surface by its strong chemical bond. This compound acted as an oxidation-protecting layer, providing an efficient combustion path to inner pure Zr particle while thermal oxidation was progressing at the same time. PVDF coating layers also made thermal reaction start at a lower temperature than ZrO₂-passivated Zr powder. It was obtained that the surface PVDF coating layer evaporated at approximately 673 K, but the surface oxide layer fully reacted at approximately 923 K by DSC analysis. Hence, Zr powders showed enhanced energetic properties by the PVDF-coated process.

Keywords: PVDF, Zirconium, Coating, Energetic Behaviors

1. Introduction

This study investigates the energetic behaviors of polyvinylidene fluoride (PVDF)-coated zirconium (Zr) powder. Zr is widely used in different fields, such as nuclear power generation, defense industry, and aerospace industry due to its high strength, high melting point, high corrosion resistance, and high flammability [1-4]. However, in the energy fields, various restrictions are placed on the surface due to the naturally formed dense oxide layer. Zr is spontaneously oxidized when exposed to air to form an oxide layer several nanometers thick on the surface. Because the oxide layer is a very thermodynamically stable material, it inhibits the reactivity of Zr. The oxide layer on the surface tends to lower the combustion efficiency of Zr [5-7]. Therefore, when the oxide layer is removed by physical or chemical methods, it could increase combustion efficiency while increasing the thermo-physical properties of Zr [8]. In this study, to improve the stability and reactivity of Zr powders, a hydrocarbon-based polymer coating process was applied to reduce the oxide layer formation of Zr and improve the reactivity at the same time [9-10]. PVDF was used as a coating material to form a polymer film. Fluorine based polymer could increase the oxidation efficiency because fluorine atoms decompose the

Zirconia shell surrounding Zr and form Zr-F coating instead of a dense oxide layer that hinders the continuous combustion reaction [11]. PVDF was chosen with those advantages as a material with high mechanical strength and good processability. It is expected to form a stable coating layer with high oxidation efficiency by having F and H atoms, which involves preparing Zr-F and Zr-F-C compounds [12-15].

2. Experimental

In this experiment, we first mixed 4.0 g of Zr powder with 60 mL of dimethylformamide (DMF) and 60 mL of 6 vol% hydrofluoric acid solutions by stirring with 150 rpm at 320 K for 5 minutes to remove naturally formed ZrO₂ film. Then, 0.8 g of PVDF was dissolved in 60 mL of DMF added to the previous etching solution by stirring with 150 rpm for 4 hours. Fig. 1 shows a schematic of the PVDF-coated Zr powder synthesis process. The synthesized PVDF-coated Zr powder was filtered using 5-um paper filters and washed with ethanol. Then, we put PVDF-coated Zr powder into thermal bake oven (Vacuum Oven, OV-11, JEIO TECH, Korea) for 24 hours at 333 K. Thermal analyzer system (TGA-DSC, TA Instruments, Discovery SDT

¹ KYUNGPPOOK NATIONAL UNIVERSITY, DEPARTMENT OF MATERIALS SCIENCE AND METALLURGICAL ENGINEERING, DAEGU 41566, REPUBLIC OF KOREA

² KYUSHU UNIVERSITY, DEPARTMENT OF MATERIALS PROCESS ENGINEERING, GRADUATE SCHOOL OF ENGINEERING, FUKUOKA, JAPAN

* Corresponding author: ijson@knu.ac.kr; bae.seonghwa.233@s.kyushu-u.ac.jp



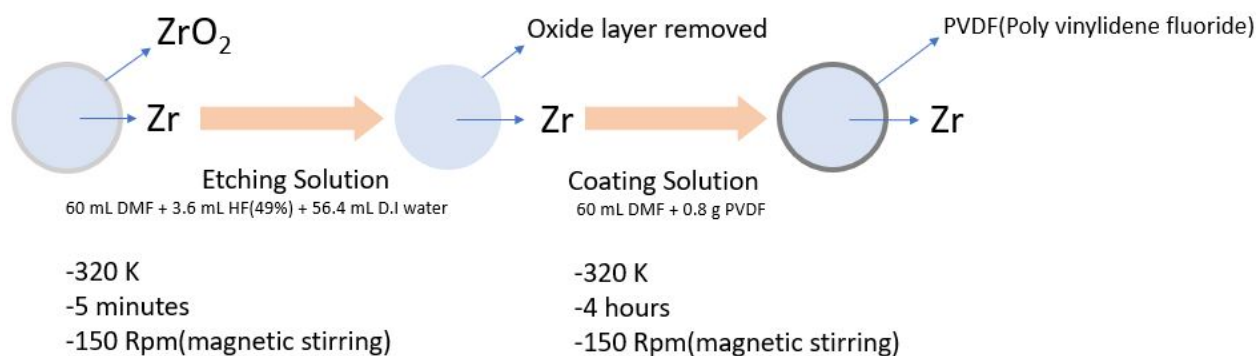


Fig. 1. Schematic of PVDF coated Zr powder synthesis process

650, USA) equipment was used to measure oxidation reactivity. PVDF-coated Zr powders were analyzed using a field emission electron probe micro-analyzer (FE-EPMA, JEOL, JXA8530F, Japan) to measure the composition of these powders. A field emission scanning electron microscope (FE-SEM, SU8220, Hitachi, Japan) was used to observe the surface of PVDF-coated Zr powders.

3. Results and discussion

Fig. 2 shows SEM images and EDS element mapping of ZrO_2 -passivated Zr powders (a, b, c), etched Zr powders (d, e, f), and PVDF-coated Zr powders (g, h, i). From ZrO_2 -passivated Zr powders (a), Zr (b), O (c) elements confirmed from EDS analysis, showing that the surface of Zr powders was covered with an

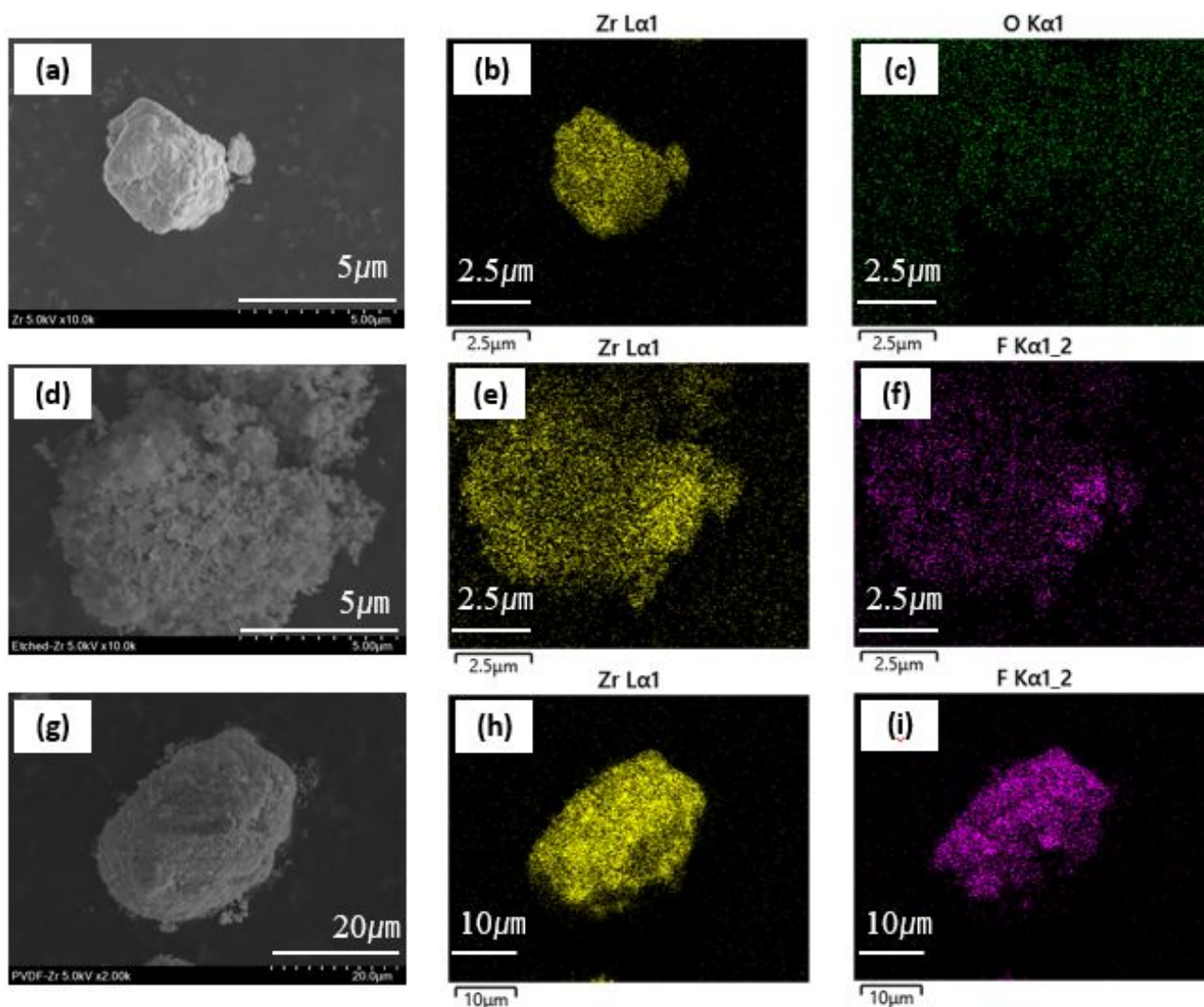


Fig. 2. SEM images of Zr (a), etched Zr (d), PVDF coated Zr powders (g) and EDS images of elements for Zr (b, c), etched Zr (e, f), PVDF coated Zr powders (h, i)

oxide film. It is also showed that the surface of the oxide layer was removed by reaction with hydrofluoric acid from the etched Zr powders (d, e, f) because Zr and F elements were detected from EDS analysis as the result of reaction with hydrofluoric acid. PVDF-coated Zr surface (g) shows a higher concentration of F elements than etched Zr powders (f). The surface layer of Zr powders was replaced from its oxide surface to PVDF-coated surface by Zr-F chemical bond.

Fig. 3 shows SEM (a) and EDS images (b, c) of cross-sectioned PVDF-coated Zr powders and FE-EPMA image and element analysis result of pressed bulk shape powders (d, e).

SEM of cross-sectioned PVDF-coated Zr powders shows a thin PVDF coating layer with slightly white color from the powder's surface. O (b) and F (c) elements are mostly located in the boundary area, suggesting that when the PVDF was coated with Zr particles, oxidation reaction occurred at the same time. FE-EPMA element analysis of pressed bulk shape PVDF-coated Zr powders showed that Zr, C, F, and O exist from PVDF-coated powders. It also suggests that oxidation reaction occurred with PVDF-coated process at the same time.

Fig. 4 shows particle size distributions of ZrO₂ passivated Zr (a), PVDF-coated Zr (b), integrated heat flow for ZrO₂

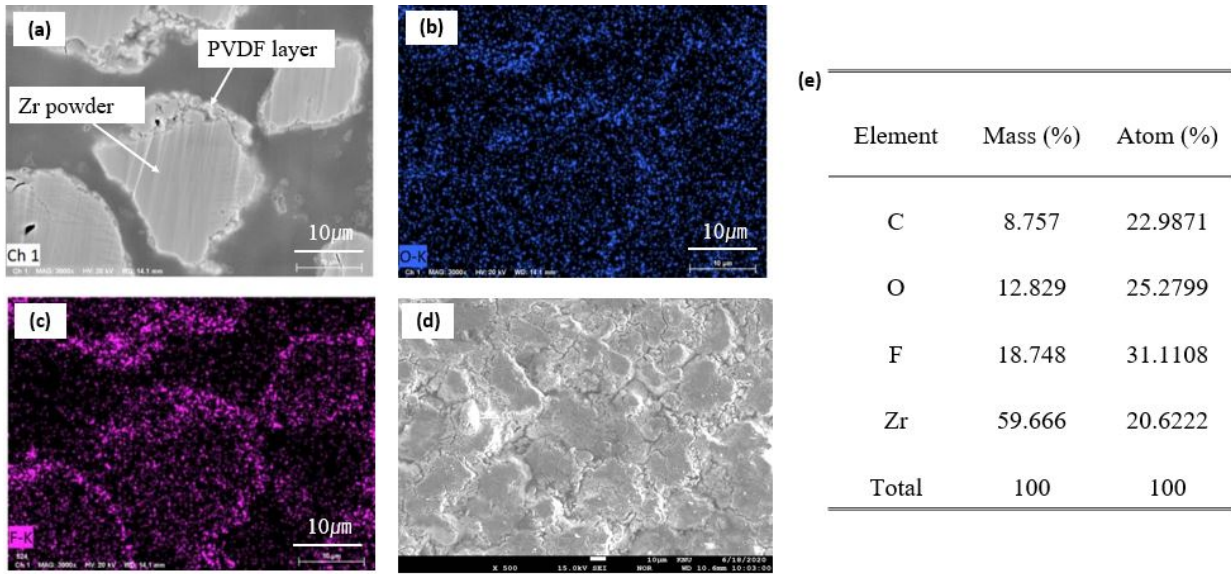


Fig. 3. SEM image (a) and EDS mapping images of O element (b) and F element (c) of cross sectioned PVDF coated Zr powders and EPMA image (d) and element analysis (e) from pressed bulk PVDF coated Zr powders

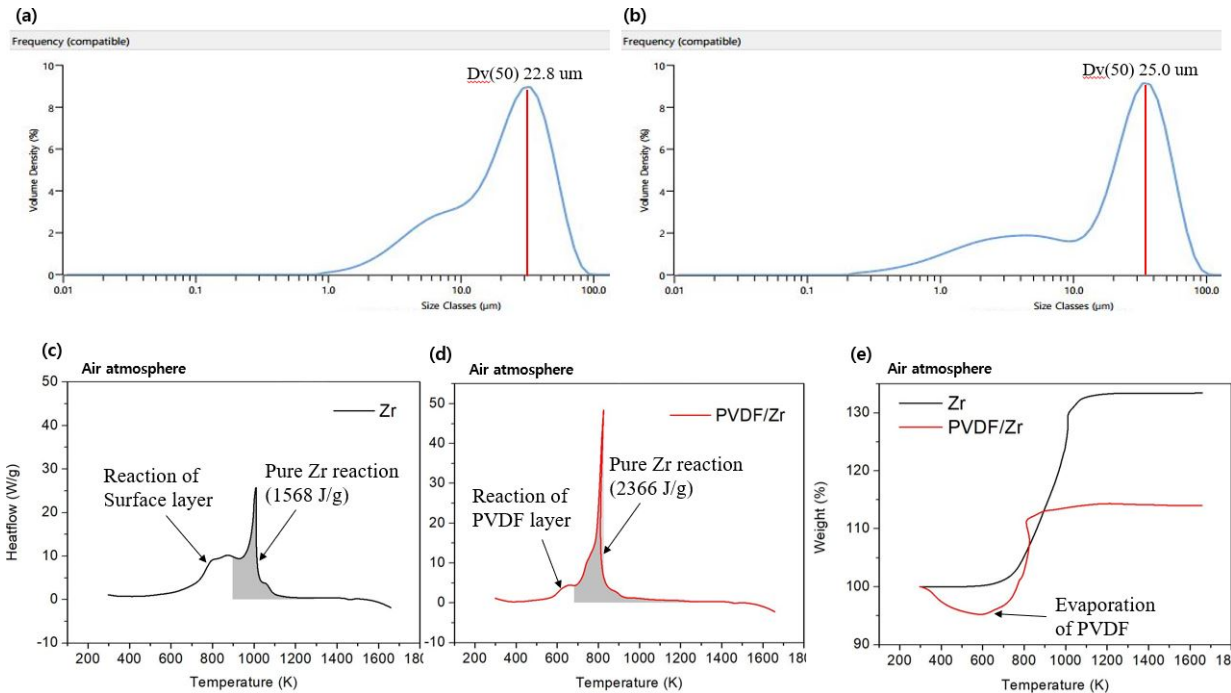


Fig. 4 Particle size distributions of ZrO₂ passivated Zr (a), PVDF coated Zirconium (b), integrated heat flow for ZrO₂ passivated Zirconium powders (c) and PVDF coated Zirconium powders (d) and TGA analysis of in ZrO₂ passivated Zr and PVDF coated Zr powders (e)

passivated Zr powders (c) and PVDF-coated Zr powders (d), and TGA analysis of in ZrO₂ passivated Zr and PVDF-coated Zr powder (e). Average particle sizes of ZrO₂ passivated (a) and PVDF-coated (b) Zr powders were 22.8 and 25.0 μm, respectively. PVDF-coated Zr particle size is bigger than ZrO₂ passivated Zr particle size since the thicker PVDF coating layer replaced 1-2-nm thickness of oxide layer on its surface. The first peak from the DSC result of ZrO₂ passivated (c) and PVDF-coated (d) Zr powders shows oxidation reaction heat flow of Zr surface. The temperature of the first peaks was 923 and 673 K, respectively, and shifted to a lower temperature direction by the PVDF coating process. When the surface oxide layer reacted fully, the inner Zr particle started reacting with oxygen to form ZrO₂, showing the second peak. Exothermic reaction heat amount of ZrO₂ passivated (c) and PVDF-coated (d) Zr powders were 1568 and 2366 J/g, respectively. When the surface PVDF coating layer evaporated fully, the oxidation reaction of the inner Zr particle progressed rapidly. TGA analysis (e) of ZrO₂ passivated and PVDF-coated Zr powders showed losing weight region at approximately 573 K. The ZrO₂ passivated Zr powders showed only weight increase due to the thermal oxidation of Zr surface. There is a the saturation weight difference between Zr and PVDF/Zr, and this is because when the oxidation layer removed, inner Zr particle also losing its surface area in PVDF/Zr.

4. Conclusion

In this study, Zr powders were coated with PVDF using a fluoride reaction. The synthesized PVDF-Zr powders showed that PVDF is adsorbed with pure Zr by a strong chemical bond as a Zr-F. The results of the thermal analyzer system (DSC) of ZrO₂-passivated Zr powders had 1568 J/g of exothermic reaction heat. However, PVDF-coated Zr powders had about 1.5 times higher of 2366 J/g. These results suggested that the naturally formed dense oxide layer required more energy to react with oxygen in the air and had inner Zr particles react slowly with lower energetic behaviors. PVDF coating layer was evaporated at approximately 573 K, and this reaction made a path where inner Zr particle rapidly encounters external oxygen atoms.

Thus, when the dense oxide layer is replaced from Zr particle to PVDF-coated powders, Zr powders were converted to more energetic materials.

REFERENCE

- [1] Y. Cao, H. Su, L. Ge, Y. Li, Y. Wang, L. Xie, B. Li, J. Hazard. Mater. **365**, 413–420 (2019).
- [2] K.R. Overdeep, H. Jores, L. Zhou, K.J.T. Livi, S.C. Barron, M.D. Grapes, K.S. Shanks, D.S. Dale, M.W. Tate, H.T. Philipp, S.M. Gruner, T.C. Hufnagel, T.P. Weihs, Combust. Flame. **191**, 442–452 (2018).
- [3] H. Nersisyan, B.U. Yoo, S.C. Kwon, D.Y. Kim, S.K. Han, J.H. Choi, J.H. Lee, Combust. Flame. **183**, 22–29. (2017)
- [4] K.R. Overdeep, K.J.T. Livi, D.J. Allen, N.G. Glumac, T.P. Weihs, Combust. Flame. **162**, 2855-2864 (2015).
- [5] D.W. Kim, K.T. Kim, G.H. Kwon, K. Song, I. Son, Sci. Rep. **9**, 1-8 (2019).
- [6] D.W. Kim, K.T. Kim, T.S. Min, K.J. Kim, S.H. Kim, Sci. Rep. **7**, 1-9 (2017).
- [7] K.T. Kim, D.W. Kim, C.K. Kim, Y.J. Choi, Mater. Lett. **167**, 262-265 (2016).
- [8] J. Dai, D.M. Sullivan, M.L. Bruening, Ind. Eng. Chem. Res. **39**, 3528-3535 (2000).
- [9] C.A. Crouse, C.J. Pierce, J.E. Spowart, ACS Appl. Mater. Interfaces **2**, 2560-2569 (2010).
- [10] O. V. Kravchenko, K.N. Semenenko, B.M. Bulychev, K.B. Kalmykov, J. Alloys Compd. **397**, 58-62 (2005).
- [11] C.E. Bunker, M.J. Smith, K.A. Shiral Fernando, B.A. Harruff, W.K. Lewis, J.R. Gord, E.A. Gulians, D.K. Phelps, ACS Appl. Mater. Interfaces **2**, 11-14 (2010).
- [12] T. Otsuka, Y. Chujo, Polymer (Guildf) **50**, 3174-3181 (2009).
- [13] D. Dambournet, A. Demourgues, C. Martineau, S. Pechev, J. Lhoste, J. Majimel, A. Vimont, J.C. Lavalley, C. Legein, J.Y. Buzaré, F. Fayon, A. Tressaud, Chem. Mater. **20**, 1459-1469 (2008).
- [14] J. McCollum, M.L. Pantoya, S.T. Iacono, ACS Appl. Mater. Interfaces **7**, 18742-18749 (2015).
- [15] D.T. Osborne, M.L. Pantoya, Combust. Sci. Technol. **179**, 1467-1480 (2007).