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A facile synthesis and efficient thermal oxidation of polytetrafluoroethylene-coated aluminum powders

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ABSTRACT

Polytetrafluoroethylene (PTFE) films were homogeneously coated onto aluminum powders. The synthesized PTFE-coated aluminum (PTFE/Al) powders showed a microstructure of spherical Al powders covered with PTFE film of a few hundreds of nm in thickness. The PTFE/Al powders showed significantly increased gravimetric energy of 4.80 kJ g^{-1} compared to the value of 0.88 kJ g^{-1} for pure Al powders during oxidation in a temperature range of 25–1450 °C. It was found that the PTFE/Al interface mixed with oxygen and fluorine atoms provided a vigorous oxidation of the Al powders. These results clearly confirm that the PTFE layer acts as a protective layer and an oxidation helper.

Aluminum (Al) and its alloyed powders have been utilized for energetic materials such as propellants, solid fuels, and pyrotechnics due to the high thermogravimetric energy release density (31 kJ g^{-1}) generated caused by the intensive and vigorous oxidation process in an air atmosphere [1–4]. However, practical energetic applications of Al powders are often limited by dense oxide layers which form on their surface [5,6]. These layers tend to prevent the further diffusion of oxygen atoms externally at a low temperature once they form on the surfaces of the Al powders. Thus, it is not easy to achieve a continued exothermic reaction until the oxide materials are removed by melting at an elevated temperature [6].

Therefore, there have been many attempts [7–12] to achieve appropriate combinations of the formation of a surface passivation layer and the enhancement of high reactivity to external oxygen atoms and thus, optimize the energetic properties. Many studies have reported that organic agents as passivation materials should be applied as a coating onto the nano- and micro-scale Al powders [8,12,13]. In particular, epoxide [14] or perfluoroalkyl carboxyl acids [15] has been developed for the passivation of nano-sized Al powders but large-scale production of stable nano-Al powders remains a problem to be solved while also achieving superior reactivity.

Among the many organic passivation materials currently available, fluorocarbons such as polytetrafluoroethylene (PTFE or Teflon) have been of interest due to their high chemical stability caused by their carbon–fluorine chain and the rapid oxidation rates, which are accelerated by the formation of compounds such as AlF_3 phase sublimated at an elevated temperature [13,16,17]. That is, it has been reported that the formation of aluminum or carbon fluorides helps to create a new surface on Al powders through their evaporation during the oxidation process. The newly formed surface can produce a large-area reactive plane. Recently, Sippel et al. [8] showed Al agglomeration using Al/PTFE mixtures for the propellant, with the mechanism of the combustion of mixed Al/PTFE elucidated. However, there have been few results pertaining to the homogenous coating of PTFE materials on the surface of Al powders thus far, despite the high likelihood that coated PTFE can be efficiently utilized as an oxidation helper for Al powders compared to mechanically mixed substances. Once PTFE is coated onto a pure Al powder surface with a minimized oxide layer, the reactivity of the powders can be consistently improved and high chemical and thermal stability of the Al powders by protective coating can be expected.

Hence, in this study, a coating process of PTFE nanoparticles to create film on spherical Al powders is introduced. The role of the coated PTFE film in the thermal oxidation of pure Al powders is then studied through an analysis of the interfacial structure between the PTFE and the Al powders.

Commercial PTFE nanoparticles (purchased from Dyneon Co. Ltd.) approximately 200 nm in size dispersed in an aqueous solution were used as the coating materials. Spherical Al powders 45 μm in size on average synthesized by a gas-atomization process

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were used as the energetic materials. Before the coating with the PTFE nanoparticles, the oxide layer present on the Al powder surface was removed using a pH-controlled sodium hydroxide solution. The Al_2O_3 film was dissolved in a solution in the form of an Al-hydroxide-forming hydrogen gas [9]. The generated hydrogen bubbles simultaneously broke the Al_2O_3 film [6]. The Al powders after oxide removal were mixed and stirred with PTFE nanoparticles, after which the PTFE nanoparticles were attached onto the pure Al surface at an elevated temperature due to the high affinity between aluminum and fluorine atoms. The PTFE nanoparticle-attached Al powders were filtered and dried at 80° C for 1 h under an Ar atmosphere. Finally, a heat treatment of the PTFE nanoparticle-coated Al powders was applied at 300 °C and maintained for 1 h in order to coat the PTFE as a layer. The microstructures of the synthesized PTFE-coated Al powders were characterized by scanning electron microscopy (SEM, JEOL, JSM-5800). The distribution of the PTFE and Al atoms were evaluated by energy-dispersive X-ray spectroscopy (EDS) equipped in the SEM. A thermogravitational analysis (TGA, SDT Model no. Q600) and a differential scanning calorimeter (DSC, SDT Model no. Q600) were used to compare both the thermal oxidation results and the exothermic reaction behavior between the PTFE-coated Al powders and the pure Al powders. The thermal analysis was performed in an air atmosphere for thermal oxidation at a heating rate of 5 °C/min. The microstructure of the PTFE/Al interface was characterized by field emission transmission electron microscopy (FE-TEM, JEM-ARM200F). The formation of PTFE was confirmed by means of Fourier transformed infrared spectroscopy (FT-IR).

Fig. 1(a) schematically illustrates the key processes used to synthesize the PTFE-coated Al powders. The Al powders are initially dispersed in an aqueous solution including NaOH in order to remove the surface oxide. As the pH reaches a level of 9–10, Al_2O_3 can be dissolved in the form of Al hydroxide materials. The PTFE nanoparticles in the solution are added to the solution of Al powders with the minimized oxide layer. The attached PTFE nanoparticles are molten and form into a film on the pure Al powders due to the heat treatment. Fig. 1(b) shows a surface SEM image of the PTFE-coated Al powders, illustrating their spherical shape. The EDS mapping results in Fig. 1(c) show that fluorine atoms are homogeneously distributed with the Al powders. Two characteristic peaks are observed at 1150 and 1250 cm^{-1} in the FT-IR graph of PTFE as shown in Fig. 1(d) and (e). These peaks are similarly revealed for PTFE/Al powders at same wave number. In addition, bonding between carbon and oxygen atoms caused by breaking of PTFE chain is observed near 1600 cm^{-1}. This indicates that the coated materials are PTFE and that they survived even after a heat treatment at an elevated temperature.

Fig. 2(a) displays a TEM image showing the PTFE/Al interface at a low magnification. This figure reveals that the thickness of the PTFE layer is approximately a few hundred nm. The SAED patterns in the inset can be identified as the [112] zone axis of the FCC Al phase. The interfacial region marked by the white square box in Fig. 2(a) was enlarged. The EDS results displaying the distribution of the oxygen, fluorine, aluminum and carbon atoms are shown in Fig. 2(b). A highly concentrated region of oxygen, carbon and fluorine atoms was found near the PTFE/Al interface as schematically illustrated in Fig. 2(c). This indicates that carbon and fluorine atoms can be readily introduced into Al oxide film or on the surface of Al powders where the oxide layer is peeled off.

Fig. 3(a) shows a comparison of the TGA results between the PTFE/Al and the pure Al powders in the temperature range of 25–1450 °C. There is no significant change in the weight gain of the pure Al except in the region past 1000 °C, which may correspond to the oxidation of Al. Compared to the pure Al, the PTFE/Al powders show a region with 5% reduction in the weight gain from 420 °C to 900 °C (Phase II); this likely occurred because the

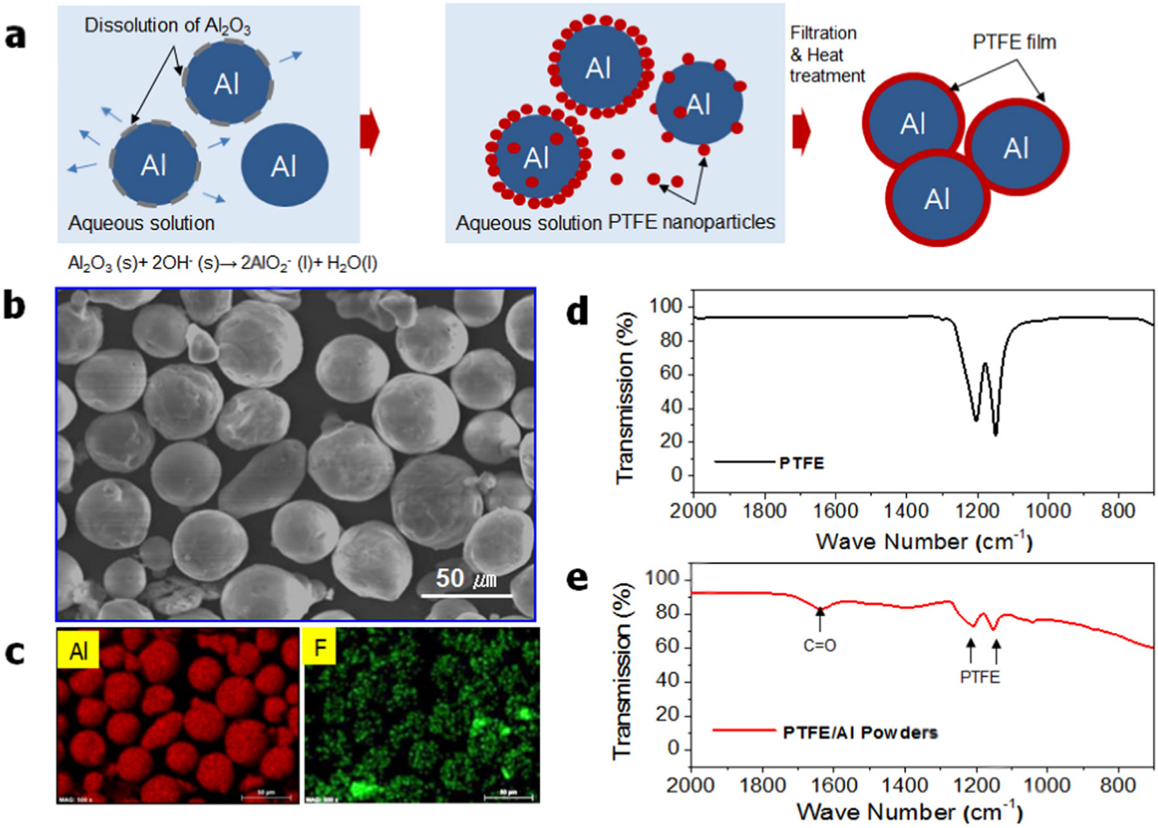

Fig. 1. (a) Schematic illustration showing the synthetic process of the PTFE/Al powders, (b) a SEM image of the synthesized PTFE/Al powders, (c) EDS results showing the distributions of aluminum and fluorine atoms, and (d) FT-IR spectral analysis of the PTFE/Al powders compared with PTFE.

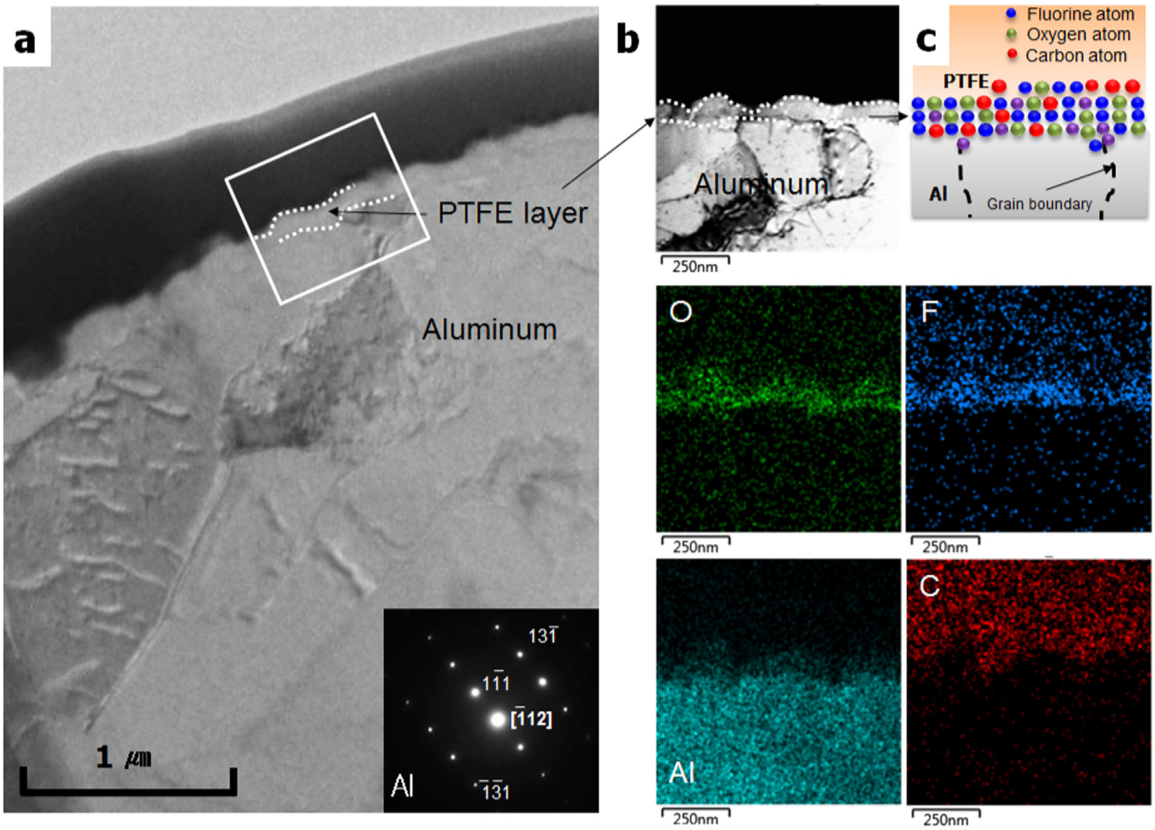

Fig. 2. (a) Cross-sectional TEM image of PTFE/Al powders, and (b) EDS results showing the distributions of oxygen, fluorine, aluminum, and carbon atoms.

surface-coated PTFE materials are molten, reacting and evaporating with the Al materials. From 950 °C (Phase III), there is a significant increase in the weight gain due to the oxidation of Al revealed after the removal of the coated PTFE and fracturing of the Al oxide film caused by the difference in the thermal expansion generated between the molten Al and the oxide film. In particular, PTFE coating provides no oxidation reaction for Al powders until the temperature reaches by 420 °C indicated as Phase I in Fig. 3(a). This indicates that PTFE materials act as a protective layer of surface oxide-removed Al powders.

Fig. 3(b) displays a comparison of the heat flow between the PTFE/Al and the pure Al powders as a function of the temperature. A small exothermic reaction peak was observed at 550 °C, which may be related to the oxidation and evaporation of the carbon or fluorine in the PTFE. The endothermic reaction peaks observed at 660 °C indicate the melting of Al in both samples. The pure Al powders shows a relatively small exothermic reaction peak near 1000 °C, which indicates that Al is changed into Al oxide by thermal oxidation. The weight gain, 107% in the pure Al powders, is significantly increased to 120% in the PTFE/Al powder. However, a significantly increased exothermic reaction peak was obtained from the PTFE/Al in the temperature range of 900–1050 °C. The enthalpy energies measured at 1100 °C from both of the DSC graphs in Fig. 3(a) are compared in Fig. 3(c). The thermogravimetric enthalpy value, 0.88 kJ g^{-1} for the pure Al powders, abruptly increases to approximately to 4.80 kJ g^{-1} for the PTFE/Al powders. This increased oxidation tendency clearly elucidates the effect of the PTFE coating for Al powders. That is, it is demonstrated here that the coated PTFE efficiently accelerates the oxidation rate of Al powders compared to that of pure Al powders with natural oxide at a relatively low temperature. On the other hand, the amount of formed Al oxide can be estimated by the enthalpy value of the Fig. 3(c) assuming all of Al is turned into only Al oxide phase. It is calculated that at least, 31% of Al in the PTFE/Al powders is transformed into Al_2O_3 but only approximately 15% of Al in the pure Al powders has been oxidized below 1450 °C.

The cause of the rapid oxidation in the PTFE/Al powders is likely the formation of new reactants such as carbonate, fluoride during the thermal oxidation process as shown in Fig. 3(d), as the formed reactants are continuously sublimated, retaining a new surface of revealed Al, which can be reacted further with external oxygen atoms supplied from the air atmosphere. This concept has been often adopted in use of Teflon-mixed Al powders [6]. Absorption onto the revealed Al surface can occur easily, generating exothermic reaction heat caused by the oxidation phenomena. Hence, a fast and vigorous exothermic oxidation process was achieved from PTFE/Al powders at a temperature below 1500 °C. Clearly, the total weight gain between the pure Al and the PTFE/Al powders will be similar at a temperature exceeding 2200 °C as the same amounts of Al-based powders are loaded. Nevertheless, the results clarify that the PTFE/Al powders shows much faster thermal oxidation than the pure Al powders due to the fluorine-added interfacial structures.

PTFE-coated Al powders were synthesized using PTFE nanoparticles in an aqueous solution. The PTFE/Al powders have a typical characteristic interfacial structure consisting of fluorine and oxygen atoms instead of the Al oxide layer which forms in a natural state. TGA results showed a higher amount of oxidation in the PTFE/Al powders, but a DSC analysis found much higher levels of exothermic enthalpy energy in the PTFE/Al powders as compared to those of pure Al powders. The rapid oxidation rate achieved with PTFE/Al powders relies on the formation of aluminum fluoride, which newly reveals the Al surface after its sublimation at an elevated temperature. Accordingly, it can be concluded that homogeneously coated PTFE plays an important role as an oxidation-protective layer as well as an oxidation helper for Al powders.

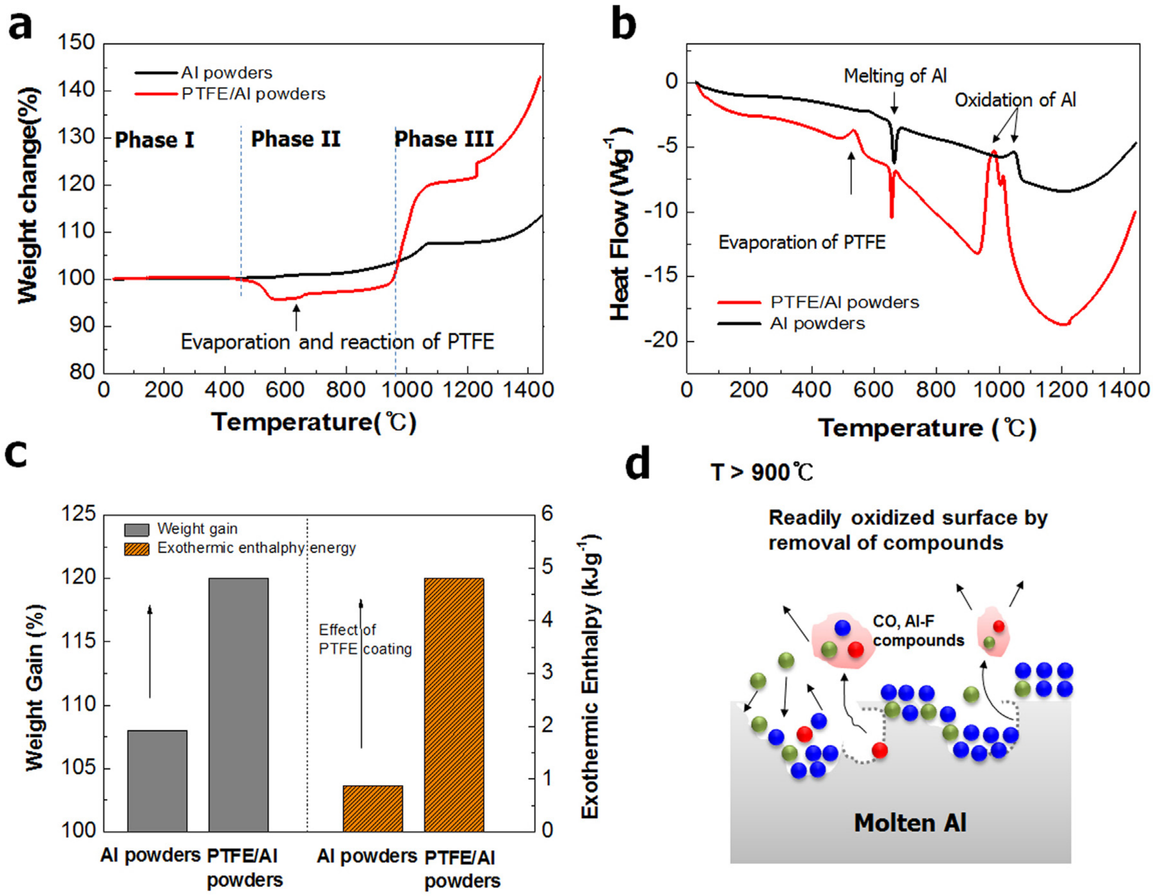

Fig. 3. Comparison of (a) TGA graphs, (b) DSC graphs between the PTFE/Al and Al powders as a function of the temperature, (c) the weight gain and exothermic enthalpy energy of the PTFE/Al powders compared to those of the pure Al powders, and (d) a schematic illustration of the oxidation mechanism of the PTFE/Al powders.

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