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EFFECT OF COMPLEXING AGENT IN NICKEL DISPLACEMENT DEPOSITION ON THE EXOTHERMIC REACTIVITY OF ALUMINUM POWDER

Aluminum powder is a representative energetic material with high heat release during oxidation. However, its performance is limited by its native oxide film. In this study, nickel displacement plating is applied to enhance the heat generation behavior of aluminum powder by utilizing the potential difference between aluminum and nickel. Citric acid, ammonium citrate, and malic acid were employed as complexing agent to control the plating behavior, and their effects on the nickel displacement plating morphology and exothermic characteristics were systematically compared. The enhanced heat generation is attributed to a self-propagating high-temperature synthesis reaction associated with the formation of Al-Ni intermetallic compounds. These results demonstrate that the choice of complexing agent is a critical factor in tailoring the reactivity of nickel coated aluminum powder for energetic applications.

Keywords: Aluminum powder; Displacement plating; Complexing agent; Exothermic reaction; Self-propagating high temperature synthesis reaction

1. Introduction

Energetic materials exhibit high heat release and rapid reaction rates during combustion, and are therefore primarily used in the aerospace and military industries. Among these materials, aluminum powder has been the most extensively adopted owing to its high gravimetric and volumetric energy density (approximately 31 kJ/g and 84 kJ/cm^3), which is superior to most other practical metallic fuels such as magnesium(approximately 14.9 kJ/g and 25.9 kJ/cm^3). [1]. The oxidation of aluminum powder is a multistep process that occurs between 573 and 1773 K, and involves the growth of amorphous alumina, the formation of γ-Al_2O_3 with accelerated oxidation, the diffusion-controlled growth of transition alumina, and finally, oxidation inhibition via the formation of dense α-Al_2O_3 [2,3]. These processes strongly govern the combustion and exothermic characteristics of aluminum. However, the naturally formed, several nanometers thick passivating Al_2O_3 layer, restricts direct contact between aluminum and oxygen, thereby increasing the ignition temperature and suppressing the oxidation kinetics. To overcome this limitation, particle size reduction and surface modification have been proposed. However, while nanosized aluminum powders exhibit enhanced reactivity due to increased specific surface area, the effective metal core can be reduced by an excessive oxide fraction and agglomeration. Consequently, aluminum powders in the 1-10 μm size range are regarded as optimal for practical energetic applications [4]. Meanwhile, surface modification by coating with fluorinated polymers and transition metals (Fe, Ni, etc.) has been shown to improve the heat dissipation performance [5,6]. In particular, nickel has attracted attention for providing an additional heat dissipation pathway due to its ability to induce a self-propagating high temperature synthesis (SHS) reaction accompanied by the formation of an intermetallic compound at the interface with aluminum [7]. Nickel displacement deposition is especially attractive, because it enables the spontaneous deposition of nickel on the aluminum surface due to the potential difference between the two metals without the need for external reducing agents. However, this process is highly sensitive to solution chemistry, particularly the stabilization of nickel ions and reaction kinetics, which are strongly influenced by the type of complexing agent. Nevertheless, systematic studies on the effect of complexing agents on the displacement nickel plating and resulting exothermic behavior of micrometer sized aluminum powders remain limited. Therefore, in this study, nickel displacement plating is applied to oxide free aluminum powders with an average particle size of 7 μm, and the effects of various complexing agents (citric acid, ammonium citrate, and malic acid) on the nickel coating morphology and exothermic characteristics

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are compared. It was expected that the type of complexing agent would influence the stability and reactivity of nickel ions in the plating bath, thereby affecting the deposition kinetics and ultimately determining the uniformity of the deposited nickel layer. A more uniform and continuous nickel layer was expected to provide a larger interfacial contact area between aluminum and nickel, promote interdiffusion and Al-Ni intermetallic formation during heating, and consequently enhance the SHS reaction and overall exothermic behavior of the aluminum powder. On the basis, the present study aimed to clarify the relationship between complexing agent, resulting nickel layer morphology, and the exothermic characteristics of aluminum powder.

2. Experimental

2.1. Surface treatment of aluminum powders

In this study, aluminum powder (MK company, Republic of Korea) with an average particle size of 7 μm was used. Prior to displacement deposition plating, chemical etching was performed by immersing the aluminum powder (3 g) in 3 wt.% aqueous hydrofluoric acid (HF; Daemyung chemical, Republic of Korea) solution for 5 min to remove the native aluminum oxide (Al_2O_3) film.

2.2. Nickel displacement deposition

The minimize re-oxidation of the aluminum surface that was exposed during the etching process (Section 2.1), the aluminum powder was immediately transferred (without intermediate rinsing) to a nickel displacement plating bath and immersed for 30 min in the selected solution. Each solution was designed to exploit the potential difference between nickel and aluminum in order to deposit a nickel coating layer. In each case, nickel sulfate hexahydrate ($NiSO_4*6H_2O$) served as the nickel ion source at a concentration of 10 g/L (expressed as nickel equivalent). To stabilize the nickel ions and control the plating reaction kinetics, several complexing agents were investigated, including: citric acid ($C_6H_8O_7$, C.A. ; Duksan Chemicals, Republic of Korea), ammonium citrate ($(NH_4)_3C_6H_5O_7$, A.C. ; Samchun Chemical, Republic of Korea), and malic acid ($C_4H_6O_5$, M.A. ; Duksan Chemicals, Republic of Korea), with a constant concentration of 10 g/L. The pH of each solution was adjusted to 10 by using aqueous ammonia (Samchun Chemical, Republic of Korea). Subsequently, the Ni-coated powders were separated from their the solutions by using a filter equipped with a filtration pump, and then dried in a vacuum oven at 100°C for 12 h.

2.3. Characterization and analysis

The thermal oxidation behavior and exothermic properties of the Ni-coated Al powders were assessed via thermogravimetric analysis and differential scanning calorimetry (TGA-DSC, SDT 650, TA Instruments) under an air atmosphere between room temperature and 1400°C at a heating rate of 10°C/min. The surface morphologies and elemental compositions of the powders were examined by field emission scanning Electron microscopy (FE-SEM, JSM-IT700HR, JEOL) and energy dispersive x-ray Spectroscopy (EDS). The nickel content of the coated powder surface depending on the complexing agent was quantified via atomic absorption spectroscopy (AAS, ICE 3300, Thermo). The measured nickel contents were converted to nickel plating amounts for comparison

3. Results and discussion

3.1. Surface morphology of the Ni-coated Al powders

The SEM/EDS results for the various nickel-plated aluminum powders are presented in Fig. 1(a). Thus, when ammonium citrate (A.C.) is used as the complexing agent, a uniform nickel-plated layer is formed on the surface of the aluminum powders, and a continuous shell-like structure is formed that surround the Al core. Conversely, when Citric acid (C.A.) or Malic acid (M.A.) was used, nickel deposition was locally aggregated or non-uniform, indicating limited formation of a continuous core-shell structure. Fig. 1(b) illustrated the schematic diagram of the nickel displacement plating process occurring on the surface of aluminum powders. Displacement nickel deposition on aluminum powder surface occurs through a localized galvanic reaction driven by the potential difference between aluminum and nickel, in which the oxidation reaction of aluminum ($Al \rightarrow Al^{3+} + 3e^-$) and the reduction reaction of nickel ions ($Ni^{2+} + 2e^- \rightarrow Ni^0$) occur simultaneously without the application of an external current, and it is highly dependent on the chemical state of nickel ions in the solution. In the absence of a complexing agent or when the complexing ability is insufficient, the activity of free nickel ions increases, leading to rapid and localized reduction on the aluminum surface. This results in non-uniform nucleation and formation of coarse nickel particles. Conversely, as depicted Fig. 1(b), when organic complexing agents are present, nickel ions are stabilized in the form of ligand-bound complex species, effectively reducing the concentration of free nickel ions and thereby controlling the reduction reaction kinetics[8]. Fig. 1(c) compares the molecular structures of the complexing agents used in this study. Although all complexing agents contain carboxyl-based ligands, A.C. exhibits an additional stabilizing effect under alkaline conditions (pH 10) due to the presence of ammonium ions (NH_4^+). The NH_4^+/NH_3 equilibrium suppresses excessive hydrolysis and hydroxide formation of nickel ions, allowing them to remain in a stable complexed state. As a result, a uniform and continuous nickel shell structure is effectively formed on the surface of the aluminum powders[9]. For a quantitative comparison of the nickel-plated layers, the mass of nickel in each specimen can be obtained from the AAS results. Assuming a spherical alu-

minum powder particle with a uniform nickel-coated layer, the average thickness of the nickel-plating layer can be calculated using Eq. (1):

$$t = r_{Al}\left[\left(1+\frac{m_{Ni}}{m_{Al}}\times\frac{\rho_{Al}}{\rho_{Ni}}\right)^{1/3}\right]-1 \quad (1)$$

where ρ_{Ni} and ρ_{Al} are the density of nickel and aluminum, and m_{Ni} and m_{Al} are the mass of nickel and aluminum, respectively. The measured weights and calculated average thickness of nickel deposited on each sample are summarized in TABLE 1.

TABLE 1

Nickel deposition mass and calculated average Ni shell thickness of Ni-coated Al powders prepared using different complexing agents as measured by atomic absorption spectroscopy (AAS)

	Ni/Al (C.A.)	Ni/Al (A.C.)	Ni/Al (M.A.)
Ni deposition mass (mg)	57.2	67.68	18.48
Calculated Ni layer thickness (nm)	39.96	47.86	12.9

Thus, the use of A.C. as a complexing agent, yields the thickest nickel-plating layer, at ~47.86 nm, while C.A. and M.C., yield average thicknesses of 39.96 and 12.9 nm, respectively. The thickness and uniformity of the nickel layer are the key factors that govern the exothermic behavior of the Ni-coated aluminum powder. During heating, the nickel layer acts as a reactive source for Al-Ni intermetallic compound formation, and both a sufficient amount of deposited nickel and a continuous interface over the entire aluminum surface are required to generate enough intermetallic product to drive a strong SHS reaction. In the study, A.C. yielded the thickest and most continuous nickel shell, whereas C.A. yielded a somewhat discontinuous deposit and M.A. yielded the thinnest and most non-uniform one. These differences in nickel layer morphology are expected to influence the extent of Al-Ni interdiffusion and intermetallic compound formation during heating, which is directly reflected in the exothermic behavior discussed in the following Section 3.2

3.2. Exothermic behavior of Ni coated Al powders depending on complexing agents

Fig. 2(a) shows the DSC curves of nickel-plated aluminum powders with the addition of complexing agents. For pure aluminum powders, the DSC curves exhibit two relatively weak exothermic peaks alongside a distinct endothermic peak near

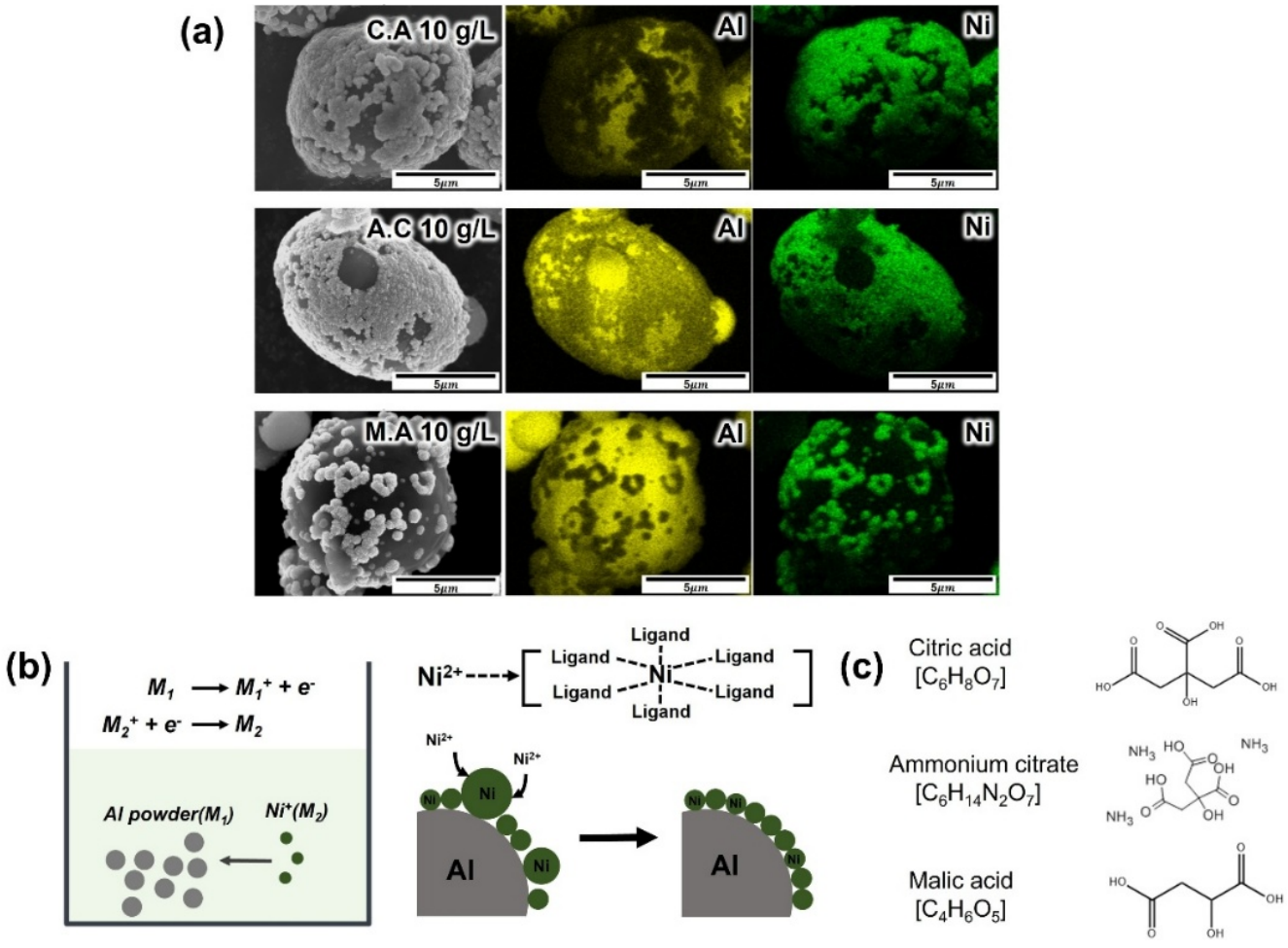

Fig. 1. SEM/EDS images of the Ni-plated Al powders that were obtained using complexing agents (a), schematic diagrams showing the nickel displacement plating process on aluminum powders (b) and the molecular structures of the complexing agents (c)

933 K, which corresponds to the melting of aluminum. The two exothermic peaks were observed at approximately 878 K (253.6 J/g) and 1309 K (1813.7 J/g), respectively. These peaks are related to the evolution, structural transformation and growth of the native aluminum oxide (Al_2O_3) layer on the powder surface during heating. Such oxide-related exothermic reactions reflect oxidation and oxide-structure-controlled thermal behavior, which dominates the heat release of pure aluminum powders and results in relatively limited exothermic performance compared to nickel-plated aluminum powders [10].

In contrast, nickel-plated aluminum powders exhibit fundamentally different thermal behavior, characterized by a distinct two-step reaction process. The first exothermic peak appears in the temperature range of approximately 850-940 K, corresponding to initial solid-state interdiffusion and interfacial reactions between the aluminum core and the nickel-plated layer near the aluminum melting point (933 K). At this stage, interdiffusion occurs along the Al-Ni interface before the aluminum core has completely melted, resulting in an early-stage interfacial reaction that is absent in pure aluminum powders. A second exothermic peak appears around 1262-1269 K and corresponds to the strong exothermic reaction caused by the SHS reaction occurring between the molten aluminum core and the solid nickel shell. When the aluminum core melts during heating, the molten aluminum comes into direct contact with the surrounding nickel shell. This results in rapid atomic diffusion at the Al-Ni interface and the formation of Al-Ni-based intermetallic compounds. The SHS reaction generates significantly more heat than the initial solid-state diffusion reaction and dominates the thermal behavior of nickel-plated aluminum powders [11]. Comparing heat generation according to the type of complexing agent reveals clear differences in the magnitude of the exothermic reactions. Under C.A. conditions, a low-temperature exothermic peak of 85.9 J/g was observed at around 916 K, followed by a larger peak of 2418 J/g at 1,262 K. When M.A. was used, an initial peak of 92.4 J/g appeared at around 917 K, followed by a peak of 2704 J/g at 1264 K. In contrast, when A.C. was used, a low-temperature peak of 96.6 J/g emerged at 916 K. The highest heat of reaction, 2770 J/g, was observed at 1269 K. As shown in Fig. 2(b), the total reaction heat, calculated by summing the two exothermic peaks, was 2866.6 J/g under the A.C. conditions. This represents an improvement of approximately 138.7% compared to the total reaction heat of pure aluminum powder (2067.3 J/g).

3.3. Mass gain of the core-shell Ni-coated Al powders

The percentage increase in weight of the pure Al and each Ni-coated Al powder sample during the oxidation process is revealed by the TGA results in Fig. 3(a). For comparison, the theoretical increase in mass (ΔM) when aluminum is completely oxidized to Al_2O_3 is given by Eq. (2).

$$\Delta M = \frac{M_{Al_2O_3} - M_{Al}}{M_{Al}} * 100 = 88.93\% \quad (2)$$

Where M_{Al} is the initial mass of aluminum and $M_{Al_2O_3}$ is the mass of oxide. This gives a theoretical value of 88.9%. However, based on Fig. 3 (b), the weight increase of the pure Al powder is only 37%, which can be attributed to inhibition of the oxidation reaction by the dense native oxide film, the nickel-coated aluminum powders each exhibit markedly enhanced oxidation reactivity, with weight increase of 67%, 73%, and 73% in the presence of C.A., A.C., and M.A., respectively. In each core-shell aluminum-nickel powders oxidation of the nickel shell takes place first during heating, or takes part in the SHS reaction, to form an intermetallic compound via a stepwise reaction, and this product increases the oxidation reactivity of the Al core [11].

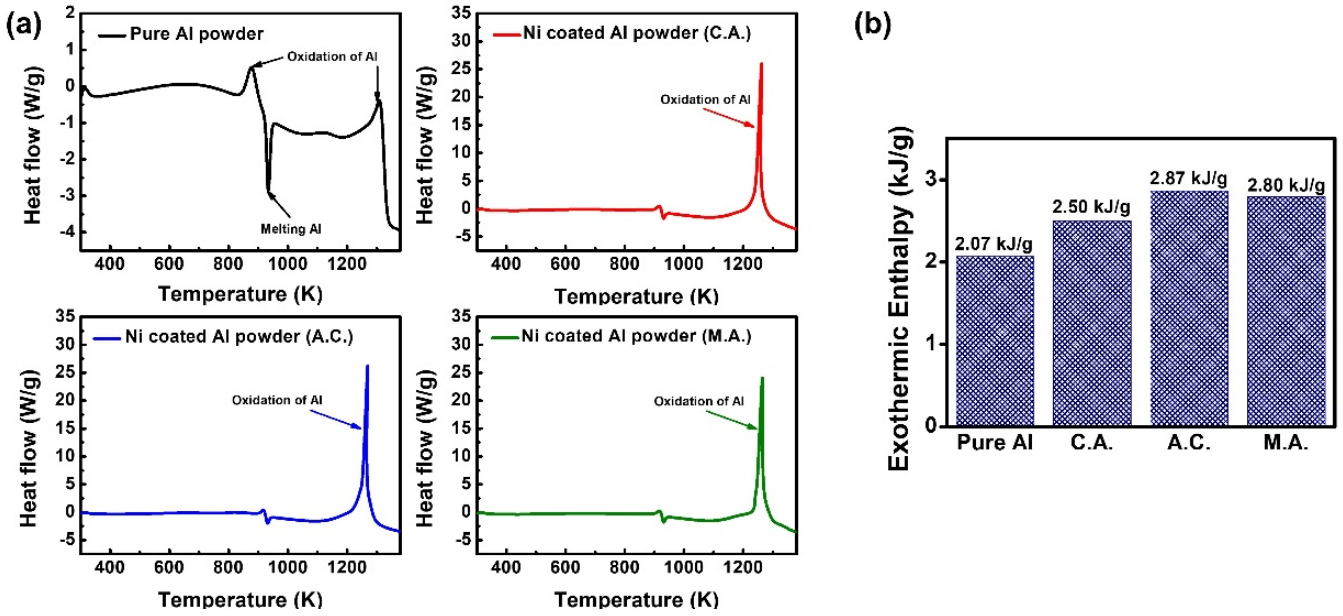

Fig. 2. The differential scanning calorimetry (DSC) curves of the pure Al powders and the Ni-coated Al powders that were obtained using various complexing agents (a), comparison of total exothermic enthalpy (b)

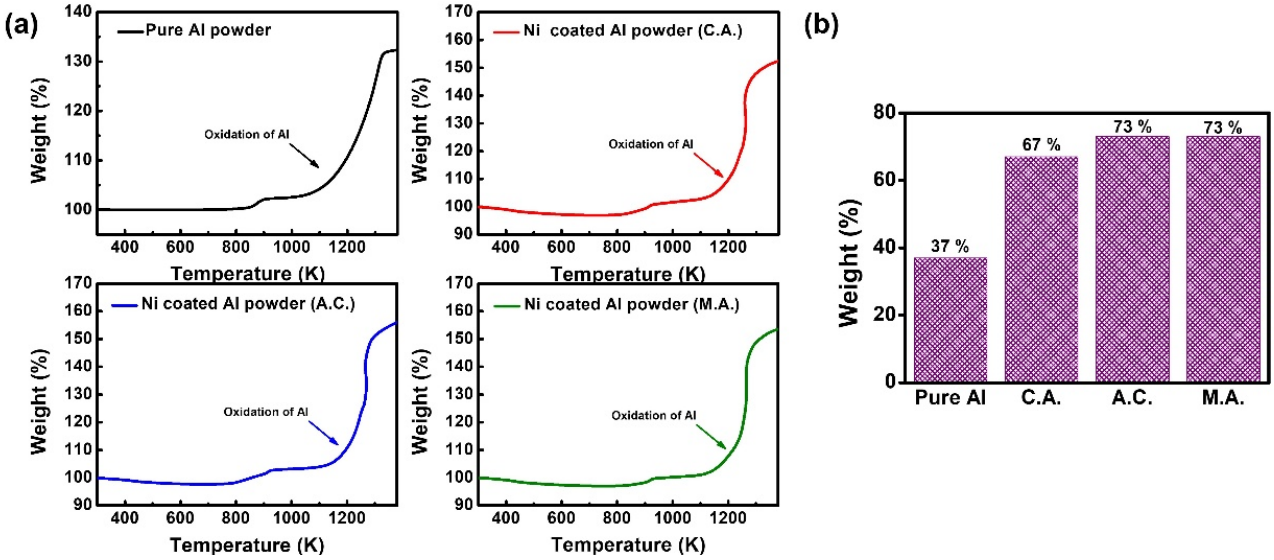

Fig. 3. The thermogravimetric analysis (TGA) results for pure Al powder and the Ni-coated Al powders that were obtained using various complexing agents (a), comparison of oxidation weight gain for each sample (b)

4. Conclusions

In this study, the changes in nickel displacement plating behavior and heat generation characteristics of aluminum powder with an average particle 7 μm were analyzed according to the type of complexing agent (citric acid, ammonium citrate, or malic acid). Thus, when A.C. was used as the complexing agent, a uniform nickel-plated shell with the highest density and an average thickness of ~47.86 nm was formed around the aluminum core. This structure maximized the Al-Ni interfacial reaction area, thereby effectively inducing the SHS reaction. As a result, the total heat generation was increased by ~138.7% compared to that of the pure Al powder.

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