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Intermetallic/Ceramic Composites Synthesized from Al–Ni–Ti Combustion with B₄C Addition

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Received: 20 May 2020; Accepted: 29 June 2020; Published: 1 July 2020

Abstract: The fabrication of intermetallic/ceramic composites by combustion synthesis in the mode of self-propagating high-temperature synthesis (SHS) was investigated in the Al–Ni–Ti system with the addition of B₄C. Two reaction systems were employed: one was used to produce the composites of xNiAl–2TiB₂–TiC with $x = 2-7$, and the other was used to synthesize yNi₃Al–2TiB₂–TiC with $y = 2-7$. The reaction mechanism of the Al–Ni–Ti system was strongly influenced by the presence of B₄C. The reaction of B₄C with Ti was highly exothermic, so the reaction temperature and combustion velocity decreased due to increasing levels of Ni and Al in the reactant mixture. The activation energies of $E_a = 110.6$ and 172.1 kJ/mol were obtained for the fabrication of NiAl- and Ni₃Al-based composites, respectively, by the SHS reaction. The XRD (X-ray diffraction) analysis showed an in situ formation of intermetallic (NiAl and Ni₃Al) and ceramic phases (TiB₂ and TiC) and confirmed no reactions taking place between Ti and Al or Ni. The microstructure of the product revealed large NiAl and Ni₃Al grains and small TiB₂ and TiC particles. With the addition of TiB₂ and TiC, the hardness of NiAl and Ni₃Al was considerably increased and the toughness was also improved.

Keywords: Al–Ni–Ti system; nickel aluminides; B₄C; self-propagating high-temperature synthesis (SHS); combustion wave kinetics

1. Introduction

Intermetallic compounds in the Al–Ni–Ti system, such as NiAl, Ni₃Al, TiAl, and NiTi, possess attractive mechanical and physical properties and are recognized as promising high-temperature materials for usage in automotive, aerospace, and turbomachinery applications [1–3]. Besides, NiTi alloys demonstrate excellent shape-memory effect, superelasticity, and biocompatibility [3,4]. However, both poor ductility and low fracture toughness hinder the extensive industrial use of Ni- and Ti-aluminides [5–7]. An effective way to improve their mechanical properties is to fabricate intermetallic-based composites, where reinforcing ceramic phases such as carbide, boride, nitride, and oxide are added [8–11].

High-energy effectivity, a shortened reaction time, operational simplicity, and a diversity of products are widely acknowledged merits resulting from combustion synthesis in the mode of self-propagating high-temperature synthesis (SHS) [12,13]. Moreover, the SHS technique represents an in situ fabrication route for the preparation of intermetallic/ceramic composites. With the use of Ni, Al, B, and Zr or Ti elemental powders as raw materials, Çamurlu and Maglia [14] synthesized ZrB₂–NiAl and TiB₂–NiAl composites using the SHS technique and reported a considerable increase in the hardness of NiAl with the addition of boride phases. Riyadi et al. [15] employed induction heating as the ignition source to initiate the SHS reaction between Ni, Al, C, and TiO₂ powders for the production of a NiAl–TiC–Al₂O₃ composite. They found an increase in the ignition temperature from 813.3 to 1133.4 K with an increasing TiO₂/Al/C content and an improvement in the hardness of

the final products containing 30–40 wt% of TiC and Al₂O₃ particles [15]. In addition, the TiAl–TiB₂, TiAl–Ti₂AlC, and TiAl–Al₂O₃ composites were fabricated by the SHS reaction using Ti/Al/B, Ti/Al/C, and Ti/Al/TiO₂ powder compacts, respectively [16–18].

It has been reported that, depending on the proportion of elemental powders, the Al–Ni–Ti system can produce a variety of intermetallic compounds via the SHS reaction, including binary phases (such as NiAl, Ti₃Al, TiAl, and NiTi) and ternary phases (such as NiAlTi, NiAl₂Ti, Ni₂AlTi, Ni₃AlTi₂, NiAlTi₂, etc.) [19]. The objective of this study was to investigate the Al–Ni–Ti combustion system with the addition of B₄C. Solid-state reaction of B₄C with Ti under the SHS mode has been confirmed to produce the TiB₂–TiC ceramic composite [20,21]. The adiabatic temperature (T_{ad}) of a combustion reaction is an important parameter for realizing the SHS process. The adiabatic temperature is the maximum temperature that a combustion process can reach without energy being lost to the surroundings and changes in kinetic and potential energies taking place. It has been empirically determined that the reaction will not be self-sustaining unless the adiabatic temperature of the reaction is higher than 1800 K [22]. The reaction of $3\text{Ti} + \text{B}_4\text{C} \rightarrow 2\text{TiB}_2 + \text{TiC}$ is highly exothermic, with a reaction enthalpy of $\Delta H_r = -753.2$ kJ [23], and a calculation based on the energy balance equation [24] gives $T_{ad} = 3245$ K. The synthesis of NiAl from the elements Ni and Al ($\text{Ni} + \text{Al} \rightarrow \text{NiAl}$) gives a T_{ad} of about 1890 K. It was noted that Ni₃Al has a larger formation enthalpy ($\Delta H_f = -153.1$ kJ/mol) than NiAl ($\Delta H_f = -118.4$ kJ/mol), but the reaction of $3\text{Ni} + \text{Al} \rightarrow \text{Ni}_3\text{Al}$ generates a lower T_{ad} of 1560 K because the heat capacity of Ni₃Al is much greater than that of NiAl [23]. Other intermetallic compounds like NiTi and TiAl can also be formed in the Al–Ni–Ti combustion system. NiTi and TiAl are formed from direct combustion of corresponding elements in a similar (i.e., weakly exothermic) manner to that of Ni₃Al, with T_{ad} values of 1583 and 1518 K, respectively [25].

In this study, the proportions between Al, Ni, and Ti powders and the molar ratio of Ti to B₄C were formulated to aim for in situ formation of the intermetallic phases (NiAl or Ni₃Al) along with the ceramic phases (TiB₂ and TiC). The effects of the sample stoichiometry on self-sustaining combustion behavior and product composition were studied. The activation energy of the combustion reaction was deduced from combustion wave kinetics. Moreover, the microstructure and mechanical properties of synthesized composites were examined.

2. Materials and Methods

The starting materials of this study included Al (<45 µm, 99.9% purity; Showa Chemical, Tokyo, Japan), Ni (<45 µm, 99.9% purity; Alfa Aesar, Ward Hill, MA, US), Ti (<45 µm, 99% purity; Alfa Aesar), and boron carbide (B₄C) (<10 µm, 99.5% purity; Showa Chemical). Two reaction systems were prepared with different elemental ratios of Ni to Al. Reaction (1) was formulated by Ni:Al = 1:1 for the formation of NiAl, and Reaction (2) had Ni:Al = 3:1 for the synthesis of Ni₃Al. On the contrary, the molar ratio of Ti:B₄C = 3:1 was the same for both reaction systems in order to produce TiB₂ and TiC at a ratio of 2:1. The parameters x and y of Reactions (1) and (2) signify the contents of NiAl and Ni₃Al to be formed in the composites; their values range from 2 to 7.

As mentioned above, the $3\text{Ti} + \text{B}_4\text{C} \rightarrow 2\text{TiB}_2 + \text{TiC}$ reaction (with $\Delta H_r = -753.2$ kJ and $T_{ad} = 3245$ K), is much more exothermic than the elemental reaction between Ni and Al. The reaction enthalpy (ΔH_r) is the difference in formation enthalpy between products and reactants. The adiabatic temperature of the reaction (T_{ad}) was calculated according to the following equation [24] (with thermochemical data taken from [23]):

$$\Delta H_r + \int_{298}^{T_{ad}} \sum n_j C_p(P_j) dT + \sum_{298-T_{ad}} n_j L(P_j) = 0 \quad (3)$$

where ΔH_r is the reaction enthalpy at 298 K; n_j is the stoichiometric constant; C_p and L are the heat capacity and latent heat, respectively; and P_j refers to the product. Consequently, it is believed that to achieve self-sustaining combustion in Reactions (1) and (2), the reaction of Ti with B_4C could be the initiation step, then followed by the metal combustion between Ni and Al.

In this study, the reactant powders were dry-mixed in a tumbler ball mill which consisted of a cylinder partially filled with raw materials and alumina grinding balls rotating about its longitudinal axis. The diameter of the grinding ball was 5 mm. The tumbler mill machine operated at 90 rpm, and the milling time was 8 h. The mixed powders were then uniaxially compressed in a stainless-steel mold at a pressure of 60–70 MPa to form cylindrical test specimens of 7 mm in diameter and 12 mm in height with a relative density of 55%. The SHS experiments were conducted in a windowed combustion chamber, which was purged and then filled with high-purity (99.99%) argon. The ignition of the powder compact was accomplished by a heated tungsten coil with a voltage of 65 V and a current of 1.5 A. The igniter coil was mounted at 2 mm above the top plane of the cylindrical sample: this can be seen in the first image of the combustion sequence shown in Figure 1. The propagation velocity of the combustion wave (V_f) was determined from the time series of recorded combustion images. The combustion temperature was measured by a Pt/Pt-13%Rh thermocouple with a bead diameter of 125 μm . The thermocouple was mounted at a position of 5 mm above the sample holder, and the thermocouple bead was firmly attached to the surface of the sample. It is believed that self-sustaining combustion had developed well when the combustion wave arrived at this position. The composition of synthesized products was analyzed by an X-ray diffractometer (Bruker D2, Billerica, MA, US) using $\text{CuK}\alpha$ radiation. Microstructure and elemental proportion were examined by a scanning electron microscope (Hitachi S3000H, Tokyo, Japan) and energy dispersive spectroscopy (EDS). Details of the experimental methods were previously reported [24,26].

Figure 1. Self-propagating combustion images recorded from Reaction (1): (a) $x = 2$ and (b) $x = 6$.

To measure hardness and fracture toughness, selected experiments were conducted by placing the powder compact in a steel mold. Densification of the product was accomplished by a hydraulic press machine under a pressure of about 300 MPa. Upon completion of the self-sustaining combustion reaction, the burned sample was quickly pressed while the product was still hot (with an estimated temperature of about 900 $^{\circ}\text{C}$) and plastic, and it was then held for about 15 s. The density of the pressed product reached about 90–93% of theoretical density. The surface of the specimen was then polished for the measurement. The relative density of the specimen after combustion sintering was determined by the ratio of the measured density to theoretical density (ρ_{TD}) of the product. The density

of the synthesized product was measured by the Archimedes method. The theoretical density of the composite was calculated from the mass fraction (Y) and density (ρ) of each component by using the following equation:

$$\frac{1}{\rho_{TD}} = \frac{Y_{NiAl}}{\rho_{NiAl}} + \frac{Y_{TiB2}}{\rho_{TiB2}} + \frac{Y_{TiC}}{\rho_{TiC}}$$

The fracture toughness (K_{IC}) of the product was determined with the indentation method using the following equation proposed by Evans and Charles [27].

$$K_{IC} = 0.16Ha^{1/2}\left(\frac{c}{a}\right)^{-3/2}$$

where H is the Vickers hardness, a is half of the average length of two diagonals of the indentation, and c the radial crack length measured from the center of the indentation. The Vickers hardness (H) was evaluated using the equation below, considering the applied load (P) and the diagonal length d (equal to $2a$) of the indentation [28]. In this study, $P = 10$ kgf was used.

$$H = 1.8544 \frac{P}{d^2}$$

3. Results and Discussion

3.1. Self-Propagating Combustion Characteristics and Kinetics

Figure 1a,b illustrates two time-sequences of recorded combustion images of Reaction (1), with one sequence showing $x = 2$ and the other showing $x = 6$, for the synthesis of NiAl-based composites. It is evident that, upon ignition, self-sustaining combustion is established and the combustion wave propagates throughout the entire sample. It took only 2.03 s for the combustion wave of Figure 1a to arrive at the bottom of the sample. With the increase of x , Figure 1b shows a longer flame-spreading time of about 6.70 s. In addition, combustion luminosity is noticeably weakened in Figure 1b when compared to that of Figure 1a. This might imply that combustion exothermicity is reduced by increasing the content of Ni and Al. As a result, the time of layer-by-layer heat transfer in the sample was prolonged. For formation of Ni₃Al-based composites in Reaction (2), the SHS process was similar to that revealed in Figure 1b, but the combustion glow was even weaker, most likely due to the fact that Ni₃Al is a less exothermic phase than NiAl.

Figure 2 presents the variation of flame-front velocities of Reactions (1) and (2) with respect to their stoichiometric parameters x and y . As shown in Figure 2, the combustion wave velocity of Reaction (1) decreases from 5.5 to 1.4 mm/s when increasing x from 2 to 7. Similarly, the combustion front speed of Reaction (2) decreases with an increase of y and drops from 3.7 to 1.1 mm/s. This decline is attributed to the dilution effect of a larger amount of Ni and Al on the overall reaction exothermicity, which is further responsible for the deceleration of the combustion front. The previous study reported that the SHS flame velocity of about 6.7 mm/s was reached by a powder compact composed only of 3Ti + B₄C [21]. Moreover, because the formation of Ni₃Al is less exothermic than NiAl, the combustion wave of Reaction (2) proceeds more slowly. Figure 2 also indicates that the difference in the flame-front velocities between two reaction systems narrows as the amounts of Ni and Al are augmented. This might suggest that metal combustion between Ni and Al gradually governs the reaction rate of the samples containing sufficiently high contents of Ni and Al.

Typical combustion temperature profiles of the powder compacts of Reactions (1) and (2) with different parameters are depicted in Figure 3a,b, respectively, both of which can reflect the combustion exothermicity. The profile features an abrupt rise in temperature to a peak value, which signifies the rapid arrival of the combustion wave and the combustion front temperature (T_c). For both reaction systems, T_c decreases when stoichiometric parameters are increased. Figure 3a shows a decrease of T_c from 1416 to 1015 °C for Reaction (1) as x increases from 2 to 7. It should be noted that the temperature

profiles of Figure 3a,b were purposely plotted away from each other in order to avoid the overlapping of the curves. As shown in Figure 3a, the profile of $x = 2$ exhibits the steepest rise in temperature among all three curves, which is attributable to its fastest combustion front.

Figure 2. Effects of Ni and Al contents on flame-front velocities of Reactions (1) and (2).

Figure 3. Effects of Ni and Al contents on combustion temperatures of (a) Reaction (1) and (b) Reaction (2).

Since Ni_3Al is a weaker exothermic phase formed by SHS, lower peak temperatures ranging from 816 to 950 °C were observed in Figure 3b for Reaction (2). It is useful to note that $T_c = 1660$ °C was detected from the SHS reaction of the $3\text{Ti} + \text{B}_4\text{C}$ sample [21]. This verifies that the SHS processes of Reactions (1) and (2) were thermally diluted by increasing Ni and Al. After the passage of the combustion wave, a significant temperature drop stemming from heat loss to the surroundings was noticed for the majority of the samples of Reaction (1), like those of $x = 2$ and 4 in Figure 3a. That is, for Reaction (1), the phase conversion of SHS was largely completed in the combustion front. However, as revealed in Figure 3b, an almost plateaued region following the maximum temperature and lasting for about 4–5 s was always observed in the temperature profile of Reaction (2). This suggests that volumetric combustion continues behind the combustion wave, perhaps because Ni_3Al is kinetically more complicated to form. According to the combustion temperature, it is suggested that Al melts at the flame front and the formation mechanism of nickel aluminides is governed by a solid–liquid reaction.

Based on an energy equation describing the combustion wave propagation and a modified Arrhenius rate function, the relationship between V_f and T_c has been derived as [29,30]

$$V_f^2 = \frac{2\lambda}{\rho Q} \frac{RT_c^2}{E_a} k_0 \exp(-E_a/RT_c)$$

where λ is the thermal conductivity, Q is the heat of the reaction, R is the universal gas constant, E_a is the activation energy of the reaction, and k_0 is a constant. The rate-controlling step of combustion synthesis is governed by chemical kinetics. The relationship between $\ln(V_f/T_c)^2$ and $1/T_c$ has been widely used to determine E_a from experimental data of V_f and T_c . By correlating a linear relationship between $\ln(V_f/T_c)^2$ and $1/T_c$, the slope of the linear line signifies E_a/R_u . Figure 4 plots two sets of experimental data with best-fit straight lines and indicates that E_a values of 110.6 and 172.1 kJ/mol are determined for Reactions (1) and (2), respectively. A larger E_a means that the reaction has a higher kinetic barrier. The composition of an intermetallic phase may vary within a restricted composition range known as a homogeneity range [31]. According to the Ni–Al binary phase diagram [5], NiAl exists in a homogeneity range from 45 to 58.5 at% Ni at 400 °C, and the homogeneity range of NiAl is found to extend from 42 to 65.5 at% Ni at 1200 °C. On the other hand, Ni₃Al has a fairly narrow homogeneity range from 73.5 to 75.5 at% Ni at 400 °C. Besides, the homogeneity range of Ni₃Al becomes more restricted (74–75 at% Ni) at 1200 °C. This suggests that NiAl is easier to form than Ni₃Al in terms of the proportion of constituent elements. From the thermodynamic point of view, the synthesis of NiAl ($T_{ad} = 1890$ K) is more exothermic than that of Ni₃Al ($T_{ad} = 1560$ K), which facilitates the SHS process of Reaction (1). Moreover, the formation enthalpy of NiAl is lower than that of Ni₃Al. This explains why Reaction (1) was determined to have a lower E_a than Reaction (2).

Figure 4. Linear correlation between combustion wave velocity and peak combustion temperature for determination of activation energies (E_a) of Reactions (1) and (2).

3.2. Phase Constituents and Properties of Synthesized Composites

Figure 5a shows the XRD patterns of the final products synthesized from Reaction (1) with $x = 2$ and 7. The as-synthesized composites consisting of NiAl, TiB₂, and TiC were identified. Figure 5a also reveals that with the increase of x , the intensity of NiAl signature peaks becomes stronger relative to those of TiB₂ and TiC, suggesting a greater content of NiAl was formed in the composite. A complete phase conversion from the reactants to desired products was also achieved in Reaction (2). Typical XRD spectra displayed in Figure 5b reveal the in situ formation of Ni₃Al, TiB₂, and TiC and an increase in Ni₃Al as the y parameter y is augmented. It should be noted that intermetallic compounds of both Ti–Al and Ni–Ti phases were not present in the final products, even though Reactions (1) and (2) involve an Al–Ni–Ti ternary system. This could be ascribed to a strong affinity between Ti and B₄C. Their reaction not only provided thermal energy to sustain the SHS process but also facilitated subsequent metal combustion between Ni and Al.

Figure 5. XRD patterns of self-propagating high-temperature synthesis (SHS)-derived products from (a) Reaction (1) with $x = 2$ and 7 and (b) Reaction (2) with $y = 2$ and 7.

Figure 6 shows the SEM micrograph and EDS spectrum of the final product of Reaction (1) with $x = 3$. The microstructure of the fracture surface reveals that micro-sized NiAl grains are subject to agglomeration into larger structures. Some TiB₂ and TiC particles are scattered over the surface, and most of them are believed to be embedded in the agglomerates. The EDS spectrum identifies all of the elements and provides a B:C:Ti:Al:Ni atomic ratio of 32.5:8.6:23.4:16.9:18.6. Among them, the ratio of Ni to Al is close to that of NiAl. The proportions of Ti, B, and C reasonably agree with the composition of 2TiB₂ + TiC.

Figure 6. SEM micrograph and EDS spectrum of the 3NiAl + 2TiB₂ + TiC composite synthesized from Reaction (1).

Regarding the product synthesized from Reaction (2) with $y = 5$, the associated SEM image and EDS spectrum are presented in Figure 7. As can be seen, large agglomerates are Ni₃Al and small grains are TiB₂ and TiC. All five elements are detected by the EDS analysis, and their B:C:Ti:Al:Ni atomic ratio is 25.2:6.2:16.9:13.5:38.2. The atomic ratio of Ni to Al confirms the intermetallic phase of Ni₃Al. The atomic ratio of Ti, B, and C is close to that of the ceramic phases of 2TiB₂ + TiC.

Figure 7. SEM micrograph and EDS spectrum of the $5\text{Ni}_3\text{Al} + 2\text{TiB}_2 + \text{TiC}$ composite synthesized from Reaction (2).

Test conditions were selected and implemented in order to achieve densification of the products, enabling them to have a relative density of 90–93%. For a densified composite of $6\text{NiAl}-2\text{TiB}_2-\text{TiC}$ synthesized from Reaction (1), Vickers hardness of $H = 652 \text{ HV}$ and fracture toughness of $K_{\text{IC}} = 5.7 \text{ MPa}\cdot\text{m}^{1/2}$ were measured. For Reaction (2), a Ni_3Al -based composite of $6\text{Ni}_3\text{Al}-2\text{TiB}_2-\text{TiC}$ shows $H = 540 \text{ HV}$ and $K_{\text{IC}} = 17.5 \text{ MPa}\cdot\text{m}^{1/2}$. Compared to combustion-synthesized monolithic NiAl ($H = 306 \text{ HV}$) [15] and Ni_3Al ($H = 250 \text{ HV}$) [32], a substantial increase in the hardness of NiAl and Ni_3Al with the addition of TiB_2 and TiC was achieved. However, the hardness values of $6\text{NiAl}-2\text{TiB}_2-\text{TiC}$ and $6\text{Ni}_3\text{Al}-2\text{TiB}_2-\text{TiC}$ composites synthesized in this study were much lower than those of TiB_2 ($H \approx 2500 \text{ HV}$) and TiC ($H \approx 3200 \text{ HV}$) [33]. This could partly be caused by two composites containing a large fraction of intermetallic phase. In part, it was because the composites produced by SHS were not fully dense.

The toughness of TiB_2/TiC -supplemented NiAl and Ni_3Al was maintained. The difference in the fracture toughness between $6\text{NiAl}-2\text{TiB}_2-\text{TiC}$ and $6\text{Ni}_3\text{Al}-2\text{TiB}_2-\text{TiC}$ composites is ascribed to the intrinsic property of two intermetallic phases. According to Mitra [34], the Ni_3Al phase exhibits a higher fracture toughness (ca. $18.7\text{--}20.9 \text{ MPa}\cdot\text{m}^{1/2}$) than NiAl ($4.1\text{--}6.6 \text{ MPa}\cdot\text{m}^{1/2}$).

4. Conclusions

Formation of intermetallic/ceramic composites by combustion synthesis in the SHS mode was investigated in the Al-Ni-Ti system with the addition of B_4C . Two reaction systems were investigated. Reaction (1) was used to fabricate the composites of $x\text{NiAl}-2\text{TiB}_2-\text{TiC}$ (with $x = 2\text{--}7$), and Reaction (2) was used to produce $y\text{Ni}_3\text{Al}-2\text{TiB}_2-\text{TiC}$ (with $y = 2\text{--}7$). Self-sustaining combustion was achieved in both reaction systems. The synthesis mechanism was governed by the fact that there was a strong tendency for Ti to react with B_4C to produce TiB_2 and TiC during the SHS process. Consequently, the intermetallic interaction occurred mainly between Ni and Al . Because the formation of TiB_2 and TiC is more exothermic than that of NiAl and Ni_3Al , the propagation rate and temperature of the combustion front decreased with the increase of Ni and Al in the reactant mixture. Experimental results showed that Reaction (1) had higher reaction temperatures ($T_c = 1015\text{--}1416^\circ\text{C}$) but lower activation energy ($E_a = 110.6 \text{ kJ/mol}$) than Reaction (2), for which $T_c = 816\text{--}950^\circ\text{C}$ and $E_a = 172.1 \text{ kJ/mol}$. This explains why Reaction (1) proceeds with higher combustion velocities than Reaction (2).

The XRD analysis showed complete conversion from the reactants to the products composed of both intermetallic (NiAl or Ni_3Al) and ceramic (TiB_2 and TiC) compounds. Ti-Al and Ti-Ni intermetallic phases were not found to be formed in the final products, which substantiated two distinct reaction paths: Ti reacts with B_4C and Ni reacts with Al . The morphology of the composite features

large Ni–Al agglomerates and dispersed small TiB₂ and TiC grains. The hardness of NiAl and Ni₃Al was considerably increased by adding TiB₂ and TiC, and their toughness was also improved.

Author Contributions: Conceptualization, C.-L.Y.; methodology, C.-L.Y. and C.-Y.K.; validation, C.-L.Y. and C.-Y.K.; formal analysis, C.-L.Y. and C.-Y.K.; investigation, C.-L.Y. and C.-Y.K.; resources, C.-L.Y.; data curation, C.-L.Y. and C.-Y.K.; writing—original draft preparation, C.-L.Y. and C.-Y.K.; writing—review and editing, C.-L.Y. and C.-Y.K.; supervision, C.-L.Y.; project administration, C.-L.Y.; funding acquisition, C.-L.Y. All authors have read and agreed to the published version of the manuscript.

Funding: This research work was funded by the Ministry of Science and Technology of Taiwan under the grant of MOST 108-2221-E-035-026.

Acknowledgments: The authors thank the Precision Instrument Support Center of Feng Chia University for providing facilities for materials analysis.

Conflicts of Interest: The authors declare no conflicts of interest.

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