Phase Formation and Interfacial Phenomena of the In-Situ Combustion Reaction of Al-Ti-C in TiC/Mg Composites

Ilguk Jo1,2, Seol Jeon3, Eunkyung Lee1, Seungchan Cho2 and Heesoo Lee1,3,*

1Department of Metallurgical and Materials Engineering, Colorado School of Mines, Golden, CO 80401, USA
2Functional Composites Department, Composites Research Division, Korea Institute of Materials Science, 797 Changwondaero, Seoongsan-gu, Changwon, 641-831, Republic of Korea
3School of Materials Science and Engineering, Pusan National University, Busan, 609-735, Republic of Korea

Phase formation and interfacial characteristics through the combustion reaction of Al-Ti-C system were investigated, in terms of the reaction mechanism. The phase formation in the reaction system at 650, 660, and 670°C by in-situ high temperature X-ray diffraction (HT-XRD) showed the formation of the solid Al3Ti phase, along with melting of the Al at 660°C. Microstructural analysis of the Al-Ti-C system after holding at 670°C was carried out to identify the reaction mechanisms, which were the formation and growth of the Al3Ti phase by dissolving Ti in molten Al. This phase occurs with further contact with C, and would initiate the combustion reaction to produce a more thermodynamically stable TiC phase. Mg-infiltrated 3.04 mm in the Al-TiC substrate was compared to 5.42 mm in the Al-Ti-C system, at the same time and temperature from the infiltration test. The apparent activation energy obtained for Al-TiC system was 350.84 kJ/mol, which was higher than that of the Al-Ti-C system (307.31 kJ/mol). The formation of the Al3Ti phase in the Al-Ti-C system was also observed from the crystal structural analysis on the infiltrated area; therefore, the in-situ combustion reaction in Al-Ti-C system promoted the wetting of Mg.

(Received September 12, 2014; Accepted January 22, 2015; Published April 25, 2015)

Keywords: titanium carbide/magnesium, metal matrix composite, in-situ combustion synthesis, reaction mechanism, aluminum-titanium-graphite system, infiltration

1. Introduction

Mg-based lightweight composites are becoming more important for industrial applications, due to their damping capacity, low density, and good castability.1) The mechanical properties of these composites depend on the characteristics of the interface between the matrix and the reinforcement.2) The metal matrix composites (MMCs) that are produced by the in-situ process exhibits better mechanical properties, as compared to MMCs produced by the conventional process, because of their thermodynamically stable reinforcement at a small size, as well as a clean interface between the matrix and the reinforcement.3,4)

Combustion synthesis has been used to investigate the synthesis of in-situ MMCs, in which the reinforcements are fabricated in the molten metal by exothermic reactions between the reactants.5) TiC has attracted attention for use as reinforcement materials because of its high hardness, high elastic modulus, and superior wear resistance.4) Recently, a combustion reaction of an Al-Ti-C system has been shown to be an efficient and energetically favorable method for producing TiC-reinforced Mg MMCs because production of the ceramic reinforcement by combustion reaction offers significant advantages: (1) the high reaction temperatures remove volatile impurities; (2) the high reaction rate lower operating and processing costs; and (3) fine and well dispersed ceramic reinforcements can be achieved in the matrices by controlling the reaction parameters.5–8)

A primary obstacle to the composite process is the non-wetting nature of the ceramics and the defects at the interface between the matrix and reinforcement. An understanding of the infiltration behavior and detailed phase evolution will provide information on the wetting behavior of reinforce-

*Corresponding author, E-mail: heesoo@pusan.ac.kr

ment with the molten metal.9) The TiC particle reinforced Mg composite produced by the in-situ combustion synthesis of an Al-Ti-C system has an inherently clean interface and better wettability, because of the in-situ formation of reinforcement and its intimate contact with the matrix. A homogeneous distribution of reinforcements in the matrix can also be achieved.10–12) For these reasons, the phase formation should be evaluated, through the in-situ combustion reaction and interfacial characteristics between the matrix and the reinforcement, in order to understand the combustion reaction mechanism of an Al-Ti-C system.

The objectives of this study are to investigate the phase evolution during (through) combustion reaction of an Al-Ti-C system and interfacial phenomena in the TiC/Mg composites that are produced by the in-situ combustion synthesis. In-situ HT-XRD was conducted for the Al-Ti-C system, and the obtained diffraction patterns were analyzed to identify the phase formation at an elevated temperature. The infiltration of Mg in the Al-Ti-C (in-situ process) and the TiC-Al (ex-situ process) substrate at the 670°C was carried out to evaluate the wettability of Mg with each system. A kinetic analysis on these infiltration profiles yielded the activation energies of infiltration.

2. Experimental Procedure

2.1 Materials and method

Ti powder (99.7%, <20 μm), graphite powder (99.99%, <20 μm) and, Al powder (99.5%, 1–5 μm) were prepared for the reactant. It is found that, less than 10 mass% Al in Al-Ti-C system could not initiate or maintain the combustion reaction with the temperature under 800°C.13,14) In these reasons, to investigate the phase evolution and the reaction mechanism in Al-Ti-C system, 5 mass% (no combustion reaction) and 20 mass% Al (stable combustion reaction) was
chosen. 5, 20 mass% Al and molar ratio of Ti/C = 1.0 were mixed by the acoustic mixer (LabRAM) to evaluate the phase evolution of Al-Ti-C system with different Al contents.

In-situ time-resolved HT-XRD analysis was performed on the Al-Ti-C mixture (20 mass% Al) with an X’Pert-Pro MPD PW3040/60 in order to investigate the crystal structure during phase transition, as the temperature increased from 650 to 670°C with an interval of 10°C under argon atmosphere.

The reaction mechanism of the Al-Ti-C system was analyzed to investigate the details of phase formation and evolution during the combustion reaction in the Al-Ti-C system. Powders were mixed and pressed into 25 mm diameter with 15 ± 1 mm thickness disk shaped substrate with green densities of 70 ± 3%. Prepared substrates were placed in the furnace and then held for 10 min at a temperature of 670°C, since the combustion reaction of Al-Ti-C system was initiated and finished by further increase in the temperature. After that, cross sectional region which parallel to the infiltration direction of those substrate were characterized using XRD, ESEM, and EDS analysis.

2.2 Mg infiltration

The infiltration lengths of Mg into the Al-Ti-C (in-situ) and Al-TiC (ex-situ) substrates were measured to evaluate the wettability of Mg. An Mg piece was polished to a cylindrical shape with 5 ± 0.2 mm of diameter, 4 ± 0.2 mm of height with a weight of 0.13 ± 0.005 g. The substrates were placed in the furnace in an argon atmosphere. Temperature was increased to 660°C and after 5 min of holding, the substrates were air quenched. Figure 1 shows the schematics of the infiltration experiment.

3. Results and Discussions

The experimental temperature range was set as 650~670°C, since the combustion reaction in the Al-Ti-C system initiated below 700°C, which is just above the melting point of Al (660.3°C). Figure 2 shows the HT–XRD results from the Al-Ti-C mixture (20 mass% Al) at room temperature, 650, 660, and 670°C. The crystal structure shown at 25°C and 650°C was in the Al and the Ti phase. However, with a temperature of 660°C and above, the Al3Ti phase was detected. The Al3Ti formation temperature corresponds to the Al melting temperature.

Figure 3(a) shows the microstructure of the Al-Ti-C (5 mass% Al) system after holding at a temperature of 670°C. Part of a non-reacted Ti particle was observed, along with the Al and C phase. The formation of the Al3Ti phase occurs in a limited local area by adding a small amount of Al, which was attributed to an insufficient amount of Al to absorb the Ti to form the Al3Ti phase. Figure 3(b) shows the microstructure of the Al-Ti-C system with 20 mass% Al after holding at 670°C for 10 min, and the result shows the existence of a blocky-shaped Al3Ti phase with sizes around 20 µm (spectra a). The small phases in contact with the Al3Ti were observed and were identified as graphite through EDS analysis (spectra b). Based on the structural and the microstructural analysis it was determined that the reaction in the Al–Ti–C system can be divided into two steps. The first step is the formation of Al3Ti (Step 1). When the Al melts, the C and Ti powders become surrounded by molten Al, followed by dissolution of Ti into the Al melt, and the formation of Al3Ti which will be in contact with the C
The heat generated by the Al-Ti reaction triggers the combustion reaction between the C and the Ti in the Al$_3$Ti to form thermodynamically more stable TiC phase ($\Delta H_f = -186$ kJ/mol) compared to the Al$_3$Ti phase ($\Delta H_f = -142.26$ kJ/mol). This reaction is highly exothermic and, the end result is the formation of TiC and Al as final products (Step 2). The details of these reaction steps are below:

Step 1: $3\text{Al} + \text{Ti} \rightarrow \text{Al}_3\text{Ti}$  
Step 2: $\text{Al}_3\text{Ti} + \text{C} \rightarrow 3\text{Al} + \text{TiC}$

Figure 4 shows the cross-sectional images of the substrate and infiltration length of Mg into the substrate, as measured by EDS point analysis. The infiltration of molten Mg initiated with the melting of Mg, and at some point, the infiltration will reach the final stage. Mg infiltrated 3.04 mm in the Al-TiC substrate, which represents the ex-situ composite process after held at a temperature of 670°C for 10 min. Compared to the Al-TiC, Mg infiltrated 5.42 mm in the Al-Ti-C system which shows the in-situ composite process at the same time, as well as the temperature.

Figure 5 shows the XRD patterns, according to the infiltrated area. The crystal structures of the infiltrated area of the Al-Ti-C substrate were Mg, Al and TiC (Fig. 5(b)); however, Mg, Al, Ti, and Al$_3$Ti phases were all detected in the Al-Ti-C substrate as shown in Fig. 5(a). These results indicate that for the Al-TiC substrate, molten Mg flows into the substrate, which is controlled by the viscosity of Mg. On the other hand, the infiltration of Mg in the Al-Ti-C substrate is promoted by chemical reaction between Al and Ti to form Al$_3$Ti. With the formation of a new solid phase at the interface, wetting of Mg occurs simultaneously. In other words, the in-situ formed TiC appears to form intimate contact with the matrix, due to the better wettability of Mg with the reactants.

Two different systems were characterized by infiltration length, with time- and temperature-dependent variations. These results make it possible to calculate the activation energy for the wetting of Mg with each substrate by performing a kinetic study from the infiltration length versus time ($dl/dt$) by applying the Arrhenius equation. The Al-Ti-C system exhibited an $E_a$ value of 307.31 kJ/mol, as compared to that of 350.84 kJ/mol from the Al-TiC system. As the infiltration is a process controlled by a chemical reaction, the TiC/Mg composite by in-situ combustion synthesis which including chemical reaction in Al-Ti-C
system would exhibits the better wettability of Mg with reinforcement.18,19)

4. Conclusion

Phase evolution of an Al-Ti-C system at an elevated temperature revealed that the reaction mechanisms involved the melting of Al, followed by the formation and growth of $\text{Al}_3\text{Ti}$. This phase then contacts with C and initiates a combustion reaction to form TiC. The infiltration lengths of Mg into the pellets have shown that Mg has infiltrated 3.04 mm in the Al-TiC substrate and 5.42 mm in the Al-Ti-C system, respectively. Infiltration length increased with time at 660°C, yielding activation energies ($E_a$) for each system and the value of $E_a$ for the Al-Ti-C system (307.31 kJ/mol) was lower than that of the Al-TiC system (350.84 kJ/mol). Phase analysis of the infiltrated area showed the formation of an $\text{Al}_3\text{Ti}$ phase in the Al-Ti-C reaction system. The formation of the novel solid phase at the interface by in-situ combustion reaction in an Al-Ti-C system promoted the wetting of the Mg. The formation of TiC occurs in Al, and as a result, TiC has intimate contact with the Mg matrix.

Acknowledgements

This work was supported by the NRF-2014R1A2A1A11051377 funded by the Ministry of Science, ICT and Future Planning (MSIP) of Korea and partially supported by a grant from the Fundamental R&D Program for Technology of World Premier Materials funded by the Ministry of Knowledge Economy, Republic of Korea. Also, this work was supported by the development program of local science park funded by the ULSAN Metropolitan City and the MEST (Ministry of Education, Science and Technology).

REFERENCES