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# The effect of a dilution agent on the dipping exothermic reaction process for fabricating a high-volume TiC-reinforced aluminum composite

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## Abstract

A synthesis of in situ formed TiC/Al composites utilizing the reaction between molten aluminum and preforms consisting of Ti, C, Al and TiC powder was studied. The addition of TiC powder as a dilution agent controlled the explosive exothermic reaction and played a key role in the homogeneous distribution of reinforcement.

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**Keywords:** Dipping exothermic reaction process; Composite; Aluminum; Microstructure

## 1. Introduction

Recently there has been a great deal of interest in the development of particulate reinforced aluminum matrix composites due their unique combination of properties such as a high specific modulus and high specific strength. The reinforcement based on TiC particulates is attractive for the aluminum matrix because of its good wettability with aluminum. Importantly, novel processing techniques based on in situ production of MMCs have

emerged in recent years [1–4]. In situ techniques involve a chemical reaction resulting in the formation of a very fine and thermodynamically stable reinforcing ceramic phase within a metal matrix. This consequently provides thermodynamic compatibility at the metal-reinforcement interface. Since the reinforced surfaces are also likely to be free of contamination, a stronger matrix-reinforcement bond can be achieved. Some of these technologies include exothermic dispersion (XD<sup>TM</sup>), reactive gas injection, self-propagating high-temperature synthesis, liquid–solid reactions and liquid–liquid reactions [5–8].

It is well known that the strength of metal matrix composites can be increased by suitably controlling the dispersion parameter, i.e. either by increasing the volume fraction or by decreasing the particle size of reinforcement. However, the

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processing of composites with high-volume fractions (>30 vol.%) of reinforcements is difficult and usually leads to structures with defects (such as cavities and cracks). In the present paper it was suggested that high-volume TiC reinforced aluminum composites could be synthesized by using a dipping exothermic reaction process (DERP) as a new processing technique utilizing the exothermic reaction between molten aluminum and preforms consisting of Ti, C, Al and TiC powder. In particular, the intent of this investigation was to evaluate the effect of a dilution agent (TiC) on the DERP.

## 2. Experimental procedure

The characteristics of constituent powders used in this work are listed in Table 1. These powders were weighed to the nominal compositions listed in Table 2, and mixed by using a Spex miller (SPEX CertiPerp Inc., Metuchen, NJ) for 10 min in the condition of dry ball milling. The preforms in this work were prepared with a hydrostatic press (100 MPa) from powders of titanium, carbon black, aluminum and titanium carbide (average particle size: 1.4  $\mu\text{m}$ ; total carbon: 19.46%; free carbon: 0.08%). The prepared preforms were dried in a

vacuum oven at 393 K for 24 h to eliminate moisture.

Fig. 1 shows the schematic representation of the DERP. The prepared preforms were cylindrical shapes, 16 mm in diameter and about 25 mm in length. To preserve the shape of the preform it was placed inside a graphite container. The graphite container was perforated with 10 mm diameter holes in the upper and bottom part for infiltrating the molten aluminum. As can be seen in the experimental setup, the specimens were dipped into the molten Al. The DERP was performed with 99.9% pure liquid aluminum. The preforms were taken out after being held for 1 min from the end point of the reaction. The end point of the reaction

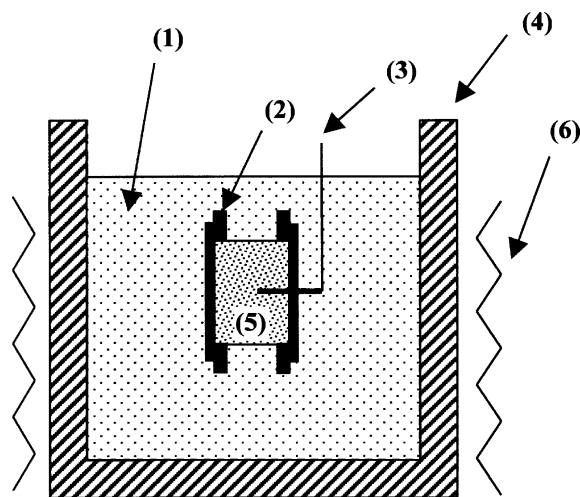


Fig. 1. The schematic representation of DERP. The sample was placed inside the graphite container to preserve the shape of the preform. (1) molten Al, (2) graphite container, (3) thermocouple, (4) crucible, (5) preform and (6) heating coil.

Table 1  
Average particle size and purity of raw powder materials

Materials	Average size ( $\mu\text{m}$ )	Purity (%)
Ti	39.63	99
C	0.7	99
Al	35.5	99.5

Table 2  
Nominal compositions of the preforms

Preform designation	Composition of preform (wt.%)			
	Ti powder	C powder	Al powder	TiC powder
A	64	16	20	0
B	56	14	20	10
C	48	12	20	20
D	40	10	20	30
E	32	8	20	40
F	24	6	20	50
G	16	4	20	60

can be determined by observing the evidence of a dazzling light that originates from the reacted preform. Optical microscopy, X-ray diffractometry and TEM were used to characterize the composites.

### 3. Results and discussion

Two categories of preforms were prepared. One consisted of element powders such as Ti, C and Al powders without TiC powders. The other consisted of elemental powders and TiC powders as a dilution agent with the composition parameters (10, 20, 30, 40, 50, and 60 wt.% TiC). Commercial

TiC powder was selected as the dilution agent due to its identity with in situ formed TiC reinforcement. The specimens of composition A (undiluted preform), and composition F (50 wt.% TiC diluted preform) are compared intensively.

Fig. 2 shows the optical micrographs of synthesized composites with variations in the amount of dilution agent and dipping temperature. The dark area of the micrograph was identified as the TiC-rich phase, and the bright area as the Al phase in SEM with EDS analysis. In the case of composition A (the preform without TiC diluents), the in situ formed TiC was distributed unevenly with big Al pockets; the uneven distribution resulted from an explosive reaction between Ti and C. At

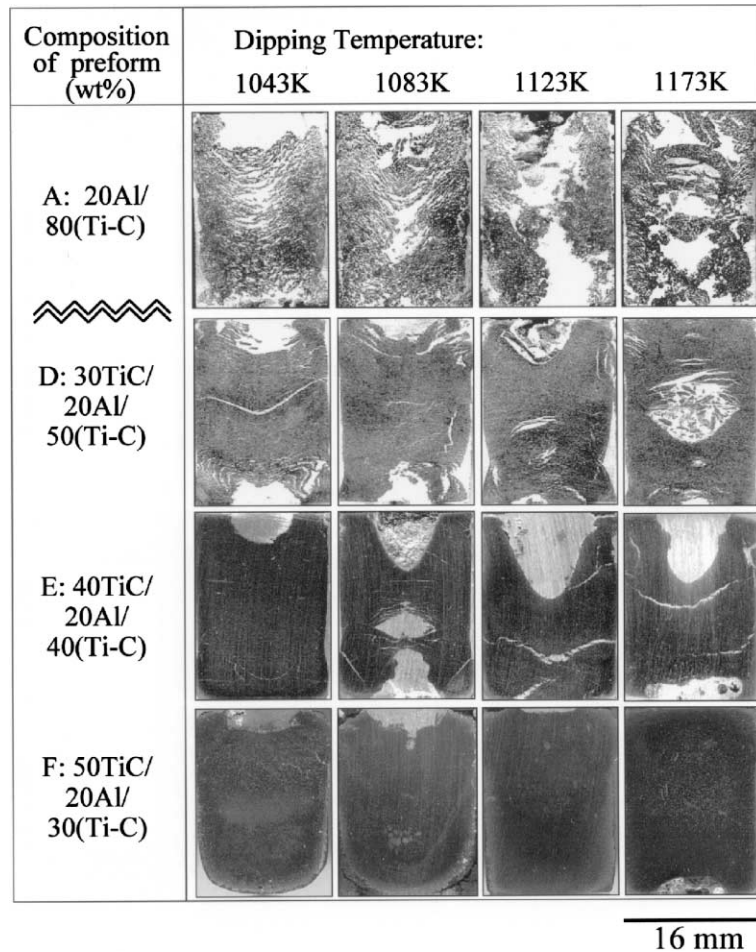


Fig. 2. The optical micrographs of synthesized composites with variations in the amount of dilution agent and dipping temperature.

the interface between the preform and the molten aluminum, TiC particles were partly detached from the preform into the aluminum melt of the crucible due to an abrupt exothermic reaction. Although the distribution of reinforcement was not homogeneous, the microstructure of the immersed specimen showed complete infiltration of the Al melt. In the case of composites with a TiC dilution agent (composites D, E and F), TiC phases were distributed more evenly than that of the preform without the dilution agent. The increase of TiC dilution gave a more homogeneous distribution of the TiC phase and the Al phase.

Fig. 3 shows the temperature profiles of preforms (compositions A and F) after being dipped into the Al melt at 1043 K. As shown in Fig. 3, the maximum temperature of the undiluted preform was about  $2090 \pm 300$  K and that of the diluted preform (with a dilution of 50 wt.% TiC) was about  $1810 \pm 100$  K. In addition, according to thermodynamic calculations [9] based on the heat capacities of Ti, C, Al and TiC [10], the theoretical adiabatic temperatures were 2780 K (undiluted preform) and 2030 K (50 wt.% TiC diluted preform) respectively. The discrepancy between the measured and calculated temperatures seemed to be due to the less perfect contact between the thermocouple and the specimen, especially in the low-diluted preform. The addition of TiC as a

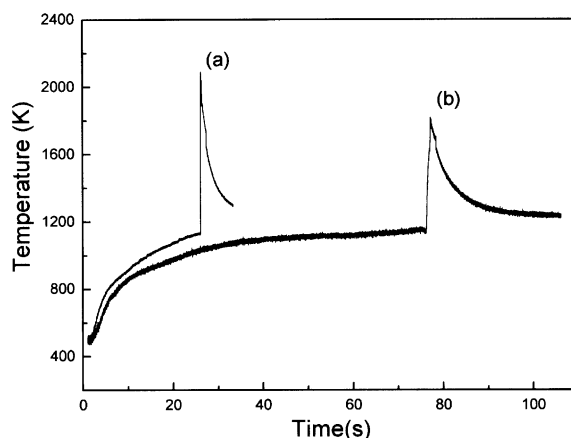


Fig. 3. The temperature profiles after being dipped into Al melt at 1043 K. (a) composition A (undiluted preform) and (b) composition F (50 wt.% TiC diluted preform).

dilution agent decreased the maximum temperature of the specimen. This decrease was due to the decrement of the exothermic reaction source (Ti and C). Nevertheless, the temperature of both specimens during the DERP increased with a sharp peak. This means that with the addition of a dilution agent the reaction in the dipping exothermic reaction was relatively explosive compared to an exemplary combustion reaction.

Fig. 4 shows the microstructure of a composite fabricated by the DERP. In the composite (Fig.

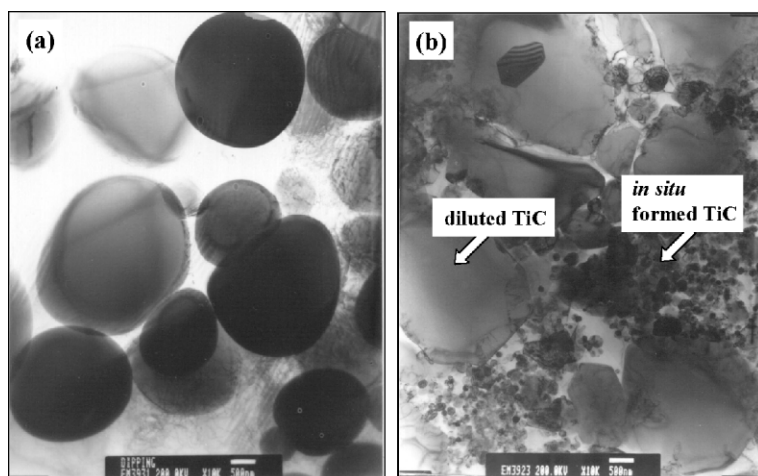


Fig. 4. Microstructures of the dipped composite after exothermic reaction at 1173 K. (a) composition A (undiluted preform) and (b) composition F (50 wt.% TiC diluted preform).

4(a)) fabricated by DERP without a dilution agent, in situ TiC particles had a round shape, which was governed by surface energy at high-temperature [11]. The average size of in situ TiC particles of the composition A (undiluted composite) is 1.3  $\mu\text{m}$  as shown in Fig. 4(a). The in situ composite (Fig. 4(b)) with 50 wt.% TiC dilution has a duplex microstructure which consists of in situ formed TiC particles (the average particle size: 0.1  $\mu\text{m}$ ) from the exothermic reaction and diluted TiC particles (the average particle size: 1.4  $\mu\text{m}$ ) from artificial addition. The size of the in situ TiC particles in Fig. 4(b) was much smaller than that of the in situ TiC particles in Fig. 4(a) (undiluted composite); this was because of insufficient time and temperature for the growth of TiC particles due to the decrease of exothermic reaction heat. As can be seen in the Fig. 4(b), although the dilution agent was added, the microstructure of the immersed specimen showed complete infiltration of the Al melt without porosity. XRD results (Fig. 5) showed that both of the composites, the undiluted (composition A) and the diluted (composition F), consisted of TiC and Al with no trace of an intermediate phase. In the case of composition F, the in situ composite with a high-volume fraction of TiC (43 vol.% TiC from EDS results) was successfully fabricated by the DERP as a one-step process.

Fig. 6 shows the changes of incubation time for exothermic reaction on the molten aluminum temperature according to variations in the amount of diluted TiC. In this study the duration of the

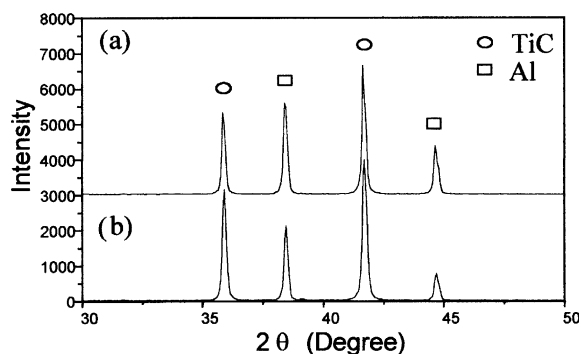


Fig. 5. XRD results of (a) composition A (undiluted preform) and (b) composition F (50 wt.% TiC diluted preform).

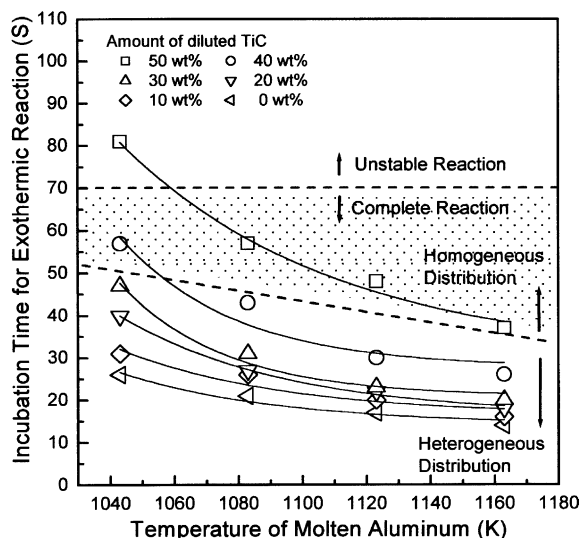


Fig. 6. The changes of incubation time for exothermic reaction on the molten aluminum temperature according to variations in the amount of diluted TiC.

incubation time for the exothermic reaction is taken from the point of putting the preform in the molten Al crucible to the point of exciting the main exothermic reaction. Depending on the increase in the temperature of molten aluminum, the incubation time for the exothermic reaction was decreased exponentially because the increase in the dipping temperature reduces the time taken to reach the ignition conditions such as the ignition temperature. These results coincided with those suggested by Todes [12] who reported that the adiabatic induction period of thermal explosion ( $t_{ad}$ ) at  $T_i$  was described by the following formula:

$$t_{ad} = \frac{RT_i^2}{E} \frac{c\rho}{Qk_0} \exp(E/RT_i) \quad (1)$$

where  $E$  is the activation energy,  $c$  is the thermal capacity,  $\rho$  is the density,  $Q$  is the heat of reaction and  $k_0$  is the pre-exponential factor of the homogeneous reaction. From Eq. (1), it follows that the adiabatic induction period of thermal explosion ( $t_{ad}$ ) has an inverse proportional relationship with the reaction heat ( $Q$ ). Furthermore, the reaction heat decreases with the decrease in the quantity of Ti and C powders, which are a source of exothermic heat. As a result, the adiabatic induction

period of the thermal explosion ( $t_{ad}$ ), which is the same as the incubation time for the exothermic reaction, has an inverse proportional relationship with the quantity of Ti and C powders. This relation coincided with the result of this experiment, as shown in Fig. 6. The longer incubation time for the exothermic reaction caused by the addition of a dilution agent is because the increment in the quantity of the dilution agent induces an increase in the average diffusion distance between the Ti and C powders through a mixing process; this makes it difficult to instigate the exothermic reaction.

In the case of a large amount of dilution agent, for example more than 60 wt.% TiC, exothermic reactions are unstable or not detected. From observation of the cross-sectioned microstructure, the boundary condition, which is satisfied with the conditions of stable reaction and homogeneous distribution for a high-volume reinforced in situ composite by the DERP, could be illustrated as in Fig. 6. This boundary condition, however, is insufficient to explain the DERP because the specimen size and the characteristics of the elemental powder change the boundary condition. Further study will be necessary to quantify the processing parameters.

#### 4. Conclusions

1. High-volume TiC-reinforced in situ Al composites were fabricated utilizing the reaction between molten aluminum and preforms consisting of Ti, C, Al and TiC powder.
2. The addition of TiC powder as a dilution agent controlled the explosive exothermic reaction and played a key role in the homogeneous distribution of reinforcement.
3. A synthesized composite obtained by the preform F with 50 wt.% TiC powder, 30 wt.% (Ti-C) and 20 wt.% Al powder consisted of TiC and Al without porosity; it had a duplex structure which consisted of in situ TiC and diluted TiC reinforcement.

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