Effect of CuO addition on microstructure and properties of aluminum composites produced by quick spontaneous infiltration process

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Abstract: Al matrix composites with a high volume fraction of reinforcements were fabricated with a compact of Al-Ti-B_4C powder mixtures by quick spontaneous infiltration (QSI) process in an aluminum melt. Given the exothermal nature of the reaction between CuO and Al, a certain amount of CuO addition to the Al-Ti-B_4C system dramatically increases the adiabatic temperature and thereby enables the complete combustion reaction in an aluminum melt (about 1,173 K). After the QSI process, the compact fabricated with CuO retains its original shape and the obtained composite exhibits sound microstructure containing reaction products of TiB_2, Al_3BC and B_4C. The formation of such reinforcements when adding CuO contributes to enhancing the properties of the composites that show far superior hardness and elastic modulus of 3.03 GPa and 158.9 GPa, respectively, with lower coefficient of thermal expansion (9.44 ppm·K^{-1}) compared to those with no CuO addition.

Key words: Al composite; CuO addition; Al-Ti-B_4C; microstructure; mechanical properties

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Aluminum metal matrix composites (MMCs) have a great potential for advanced structural applications due to their high specific strength, good elastic modulus, and desirable thermal properties [1-5]. The infiltration process is one of the most useful processes with which to fabricate composites with a high volume fraction of reinforcements. MMCs can be made in this way with good near-net-shape characteristics. In a recent study by the authors [6], a novel process of spontaneous infiltration was developed for producing aluminum matrix composites reinforced with reaction products of an Al-Ti-B_4C-CuO system. In this process, the combustion reaction in the compact was initiated via the heat absorbed from the aluminum melt and the subsequent infiltration of the aluminum melt simultaneously filled the internal pores of the compact. Differing from the former study [6] which focused on the innovative process, this study concentrated on the critical role of the CuO addition to Al-Ti-B_4C mixtures, in the combustion reaction.

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Due to its less stable nature than that of Al_2O_3, adding CuO into aluminum is one of the most common thermite reactions (the reaction heat of Al_2O_3 is -1675.7 kJ·mol^{-1})[7]. Thermite reactions, a class of oxidation –reduction reactions, can be written in a general form as:

$$M + AO = MO + A + H$$

Where M is a metal or an alloy and A is either a metal or a non-metal, MO and AO are their corresponding oxides, and H is the heat generated by the reaction [8]. Those thermite reactions are characterized by a large heat release which is often sufficient to heat the product phases above their melting point. The fact that many thermite reactions yield a molten product that consists of a heavier metallic phase and a lighter oxide phase which can be separated by gravity, makes these reactions potentially useful in a variety of metallurgical applications [9]. Also, thermite reactions have become important in the synthesis of refractory ceramic and composite materials [10].

In this study, a small amount of CuO was added and the thermite reaction is used for assisting the combustion reaction in the Al-Ti-B_4C system. To date, there are few reports [11] on the utilization of thermite reaction to assist in the other combustion reaction. Cho et al. [11] reported that the addition of CuO to an Al-Ti-C system dramatically increased the theoretical adiabatic temperature and was beneficial in reducing the aluminum melt temperature to approximately 1,073 K when fabricating Al-TiC composites in an aluminum melt.

In the present study, the effect of CuO addition to an Al-Ti-B_4C powder mixture on the microstructure and mechanical properties of aluminum composites produced by QSI process was investigated. An important role of CuO addition in the combustion reaction among Al-Ti-B_4C system in the QSI process was further discussed.

1 Experimental procedure

The starting raw powders used in the experiments were as follows: Ti (99.5%, 50 μm), Al (99.5%, ~30 μm), B_4C (99.5%, 15 μm), and CuO (99.95%, ~10 μm). To study the effect of CuO addition, the reagent powders were mixed at a proper mole ratio (Ti: B_4C: Al: CuO = 3: 4: 6: 0.4 and Ti: B_4C: Al = 3: 4: 6) for an hour and then compacted at room temperature into a cylindrical shape to make a compact (h = 28 mm, d = 35 mm, 55%–60% of the theoretical density). This was subsequently dried in an oven at 473 K for two hours to eliminate moisture. Pure aluminum ingots weighing a total of 800 g were melted in a graphite crucible using an electric resistance furnace. The compacts, which weigh 40–50 g each, were placed inside a graphite tube mold [6] and then submerged in the aluminum melt at about 1,173 K. The compacts were ignited in the aluminum melt, with subsequent spontaneous infiltration towards them. Approximately four minutes later, each compact was taken out from the melt and cooled in air.

The obtained compacts were wire-cut to inspect their cross-sections. The compacts for microstructure observation were mechanically polished and then analyzed using FE-SEM (JSM-7100F) and EPMA (Electro-Probe Microanalyzer). An X-ray diffraction (XRD) analysis with Cu Kα radiation was also carried out to identify the phases. To monitor the variation of temperature with time during the process, a small hole was drilled in the top of the compact and a C-type thermocouple pair was inserted into the hole. The other end was linked to an X-Y recorder. The hardness was measured by an XTC_{am}-D300 microhardness tester, and the elastic modulus was obtained by a resonant ultrasound spectrometer. The coefficient of thermal expansion (CTE) was measured using a DIL402C dilatometer system.

In addition, differential thermal analysis (DTA) was performed on the two kinds of compacts at the mole ratio (Ti: B_4C: Al: CuO = 3: 4: 6: 0.4 and Ti: B_4C: Al = 3: 4: 6) to assist the investigation of the effect of CuO addition. Powder mixtures were not used directly, instead pressed into a small compact (h = ~6 mm, d = 3 mm, ρ = 55%-60%, m = ~75 mg) to match the DTA crucible. The compacts were heated from 313 K to 1,773 K at a rate of 10 K·min^{-1} under argon atmosphere.

2 Results and discussions

2.1 Microstructure

Figure 1 shows the cross-sections of the two compacts using the reactants with/without CuO addition by the quick spontaneous infiltration process. In the compact fabricated without CuO, it was found that the bottom part of the compact crumbled into the melt whereas the compact fabricated with CuO shows a sound shape. This suggests that a certain amount of CuO addition significantly improves the soundness of the compact. The detailed reasoning will be explained later.

The density of the compact fabricated with CuO is 2.94 g·cm^{-3} whereas the density of the compact fabricated without CuO is 2.79 g·cm^{-3}. This suggests that the compositions of the two compacts may be very different after the combustion reaction and infiltration process. In the case of adding CuO, dazzling light can be observed during the QSI process after putting the compact into the melt for a period of time, while weak light was observed in the case of not adding CuO. This suggests that a combustion reaction took place in the compact with added CuO.

Figure 2(a, c) shows the microstructure of the composite fabricated without CuO. These figures show that Al_3Ti and B_4C are dispersed in the Al matrix. There is a very thin layer composed of TiB_2 around the B_4C particles. Figure 3(a) is the corresponding XRD result, which also shows that only Al_3Ti and B_4C exist in the composites along with a small quantity of TiB_2.

Figure 2(b, d) shows the microstructure of the composite

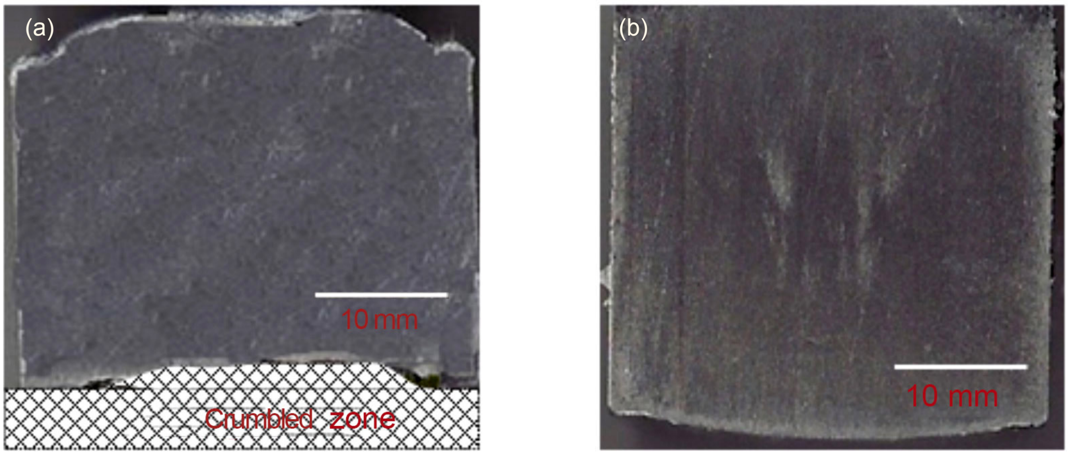
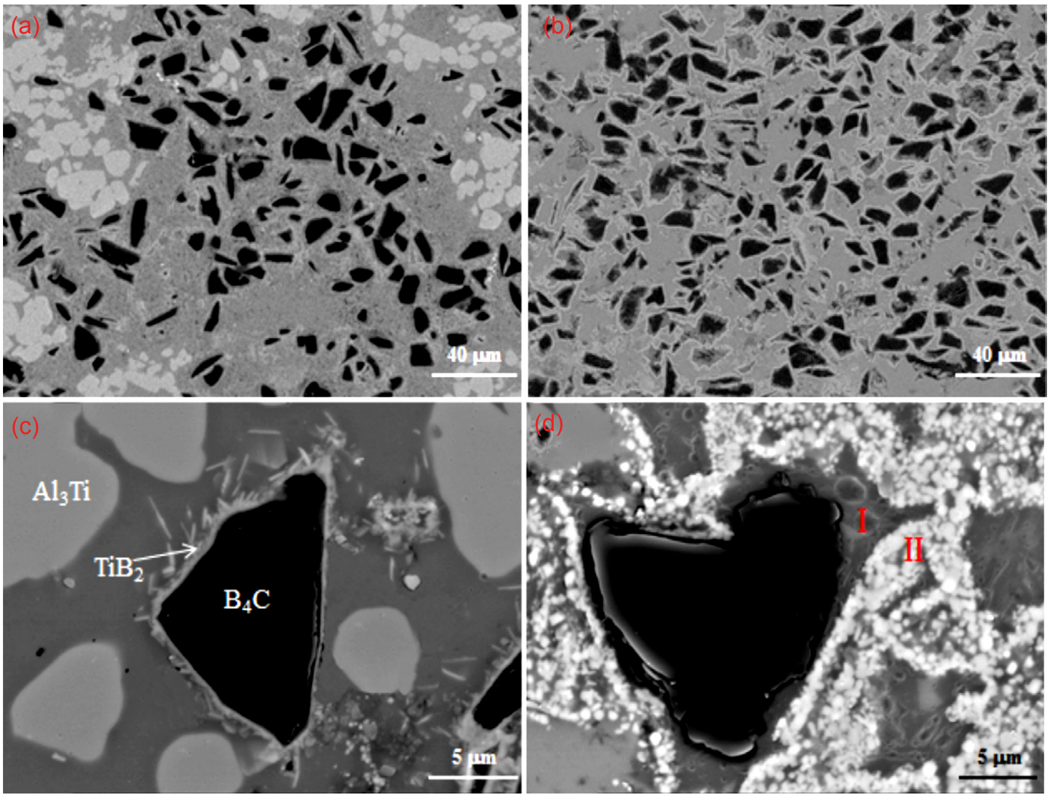


Fig. 1: Cross-sections of two compacts fabricated by QSI process: (a) without CuO, (b) with CuO



(e) EPMA (at.%)

	I	II
Al	55.64	7.19
Ti	-	30.08
B	23.51	61.32
C	20.85	1.41

Fig. 2: FE-SEM of Al matrix composites fabricated by QSI process: (a, c) without CuO, (b, d) with CuO, (e) EPMA analysis

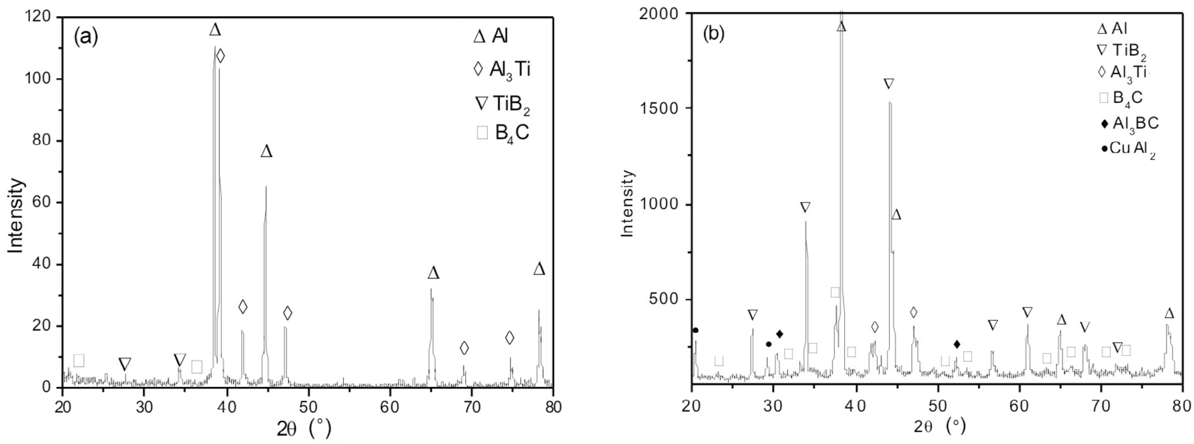


Fig. 3: XRD patterns of Al matrix composites fabricated by QSI process: (a) without CuO, (b) with CuO

fabricated with CuO. The EPMA result in Fig. 2(e) verifies that besides the remaining B_4C, products TiB_2 and Al_3BC are observed in the microstructures. Figure 3(b) is the corresponding XRD result, which also shows that B_4C, Al_3BC and TiB_2 exist in the composite.

In the CuO-free compact, as confirmed by the microstructure analysis, the reaction (1) and just a little reaction (2) take place, that is, an incomplete reaction occurred. However, both the reactions (1) and (2) react completely along with the highly exothermic reaction (3) in the compact containing CuO, that is, a complete combustion reaction occurred.

$$3Al + Ti = Al_3Ti \quad (1)$$

$$3Al_3Ti + 4B_4C = 2Al_3BC + 3TiB_2 + 2B_4C + 3Al \quad (2)$$

$$2Al + 3CuO = Al_2O_3 + 3Cu \quad (3)$$

2.2 Properties

In the composites fabricated with and without CuO, entirely different microstructures were obtained in the QSI process. In the composite without CuO, ignoring the small amount of TiB_2, the microstructures were mainly composed of B_4C and Al_3Ti and the volume fraction of B_4C and Al_3Ti was estimated to be 27.5% and 35.2%, respectively. In the composite fabricated with CuO, the microstructures were mainly composed of B_4C, TiB_2 and Al_3BC, and in our previous study [6], it was suggested that in the composite fabricated with CuO, the volume fractions of B_4C, TiB_2, Al_3BC, and Al_3Ti were estimated to be 16.3%, 10.4%, 16.4%, and 8.6%, respectively. The properties of the composites depend largely on the reinforcements in the matrix. It is therefore expected that the obtained composites fabricated with and without CuO have different properties.

The hardness of the composite fabricated with CuO is 3.03 GPa, which is much higher than that without CuO (1.70 GPa). The lower hardness of the composite fabricated without CuO may result from the presence of large amount of Al_3Ti phase having lower hardness compared to B_4C, TiB_2 and Al_3BC (Table 1).

It was reported [12] that the elastic modulus depends to a great extent on the type and volume fraction of the reinforcing particles. The elastic modulus of the concerned reinforcing particles is shown in Table 1. The elastic modulus of the composite fabricated with CuO is 158.9 GPa (shear modulus 63.7 GPa, bulk modulus 104.7 GPa), which is higher than 132.0 GPa (shear modulus 52.9 GPa; bulk modulus 87.2 GPa), the elastic modulus of the composite fabricated without CuO. Even though the volume fraction of reinforcing particles in the composites without CuO is very high, Al_3Ti, which possesses lower elastic modulus than others, decreases the elastic modulus of the composite fabricated without CuO.

Similar to the elastic modulus, the coefficient of thermal expansion (CTE) of composite is related to the type and volume fraction of the reinforcing particles. The CTE values of the two composites fabricated with and without CuO are 9.44 ppm·K^{-1} and 11.67 ppm·K^{-1}, respectively. It is suggested that due to the higher CTE value of the reinforcement Al3Ti as demonstrated in Table 1, the composite fabricated without CuO, which possesses large amounts of Al_3Ti, shows higher CTE than the composite fabricated with CuO.

Table 1: Properties of reinforcing particles in fabricated composites

Reinforcement	Density g·cm^{-3}	Hardness GPa	Elastic modulus GPa	Bulk modulus GPa	Shear modulus GPa	CTE ppm·K^{-1}	Ref.
Al_3Ti	3.36	5.65	175	117.86	71	13	[15, 16]
Al_3BC	2.66	12.1	326	152	140	6.67	[17, 18]
TiB_2	4.52	34	565	240	255	6.4	[19, 20]
B_4C	2.52	48.54	449	226	192	5.73	

3 Discussions

3.1 Effect of CuO addition on ignition of combustion reaction

Figure 4(a, b) shows the temperature profiles with time in the two compacts and corresponding aluminum melt. As shown in Figs. 4(a) and (b), the ignition delay time of the compact without CuO is longer than that with CuO. During the ignition delay time, Al and Ti powders in the outer layer of the powder compact in direct contact with molten Al tend to dissolve into the aluminum melt. A longer ignition delay time results in the crumbling of the compact without CuO, as shown in Fig. 1(a). In addition, the ignition temperature of the compact with CuO is lower than that without CuO. It can be inferred that the CuO addition is attributed to ease the ignition.

In order to verify the effect of CuO addition, DTA analysis was also performed with the same reactant powder mixtures with and without CuO. Figure 5 shows the DTA and corresponding XRD patterns of the powder mixtures with and without CuO. The results of DTA and XRD patterns are almost the same in the two compacts with and without CuO. In the DTA patterns, the endothermic peak (I) around 930 K corresponds to the Al melt, while the first exothermal peak (II) corresponds to the reaction (1) and the second one (III) to the reaction (2). The intensity of the peaks in these two composites shows no significant difference. It is noted that the starting point of the second exothermal peak in the compact containing CuO is lower than that in the CuO-free compact. It is also evident that the CuO addition is beneficial to the ignition of the combustion reaction which is demonstrated in Figs. 4(a) and (b).

It was reported that the reaction between Al and CuO [reaction (3)] started at ~843 K [17] which is very close to the ignition temperature of the compacts containing CuO. This reaction may contribute to the ignition of the Al-Ti-B_4C system in the QSI process.

3.2 Effect of CuO addition on propagation of combustion reaction

From Figs. 4(a) and (b), it is noted that the measured peak temperature of the compact containing CuO is about 330 K higher than that without CuO in the QSI process. In addition, the duration time of the combustion reaction in the compact containing CuO is also longer than the CuO-free compact. The reactions in the compact containing CuO released more heat than that in the CuO-free compact. It is proved again that a complete combustion reaction occurs in the compact containing CuO, while an incomplete combustion reaction occurs in the CuO-free compact.

In the DTA process, the results of DTA and XRD patterns are almost the same in the two compacts containing and not containing CuO as shown in Fig. 5. A tiny difference in the XRD patterns is that in the compact containing CuO, $CuAl_2$ was found in the XRD pattern, as shown in Fig. 5(b). Also, the extra small peak in the first exothermal peak (II) of the compact containing CuO [Fig. 5(a)] corresponds to the reaction (3). This suggests that in the CuO-free compact, reactions (1) and (2) occur, while in the compact containing CuO, reactions (1), (2) and (3) occur. In both the compacts with and without CuO, a complete combustion reaction occurs during the DTA process.

This brings out the question as to why the reactions of the CuO-free compact in actual QSI process is incompleted whereas that in DTA process is completed as demonstrated in Table 2, since the reactants are totally identical. This is associated with the difference between the DTA and QSI processes: no

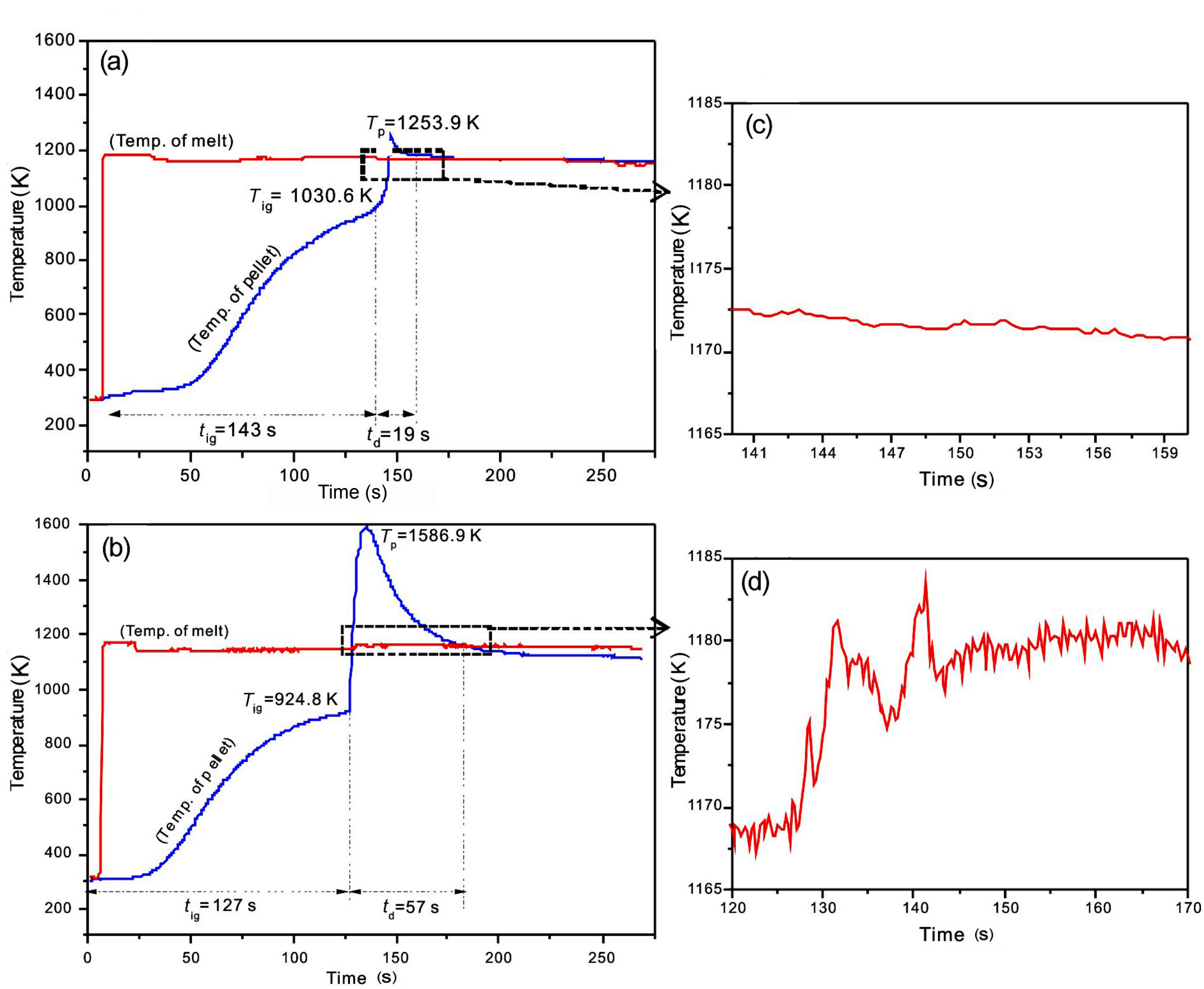


Fig. 4: Measured temperature profiles with time in compacts: (a) without CuO, (b) with CuO and the corresponding aluminum melt temperature during QSI process, (c) and (d) part of temperature-time profile of aluminum melt circled in (a) and (b), respectively. (T_p: the peak temperature; T_{ig}: the temperature at ignition; t_{ig}: ignition delay time; t_d: duration time of the combustion reaction.**)**

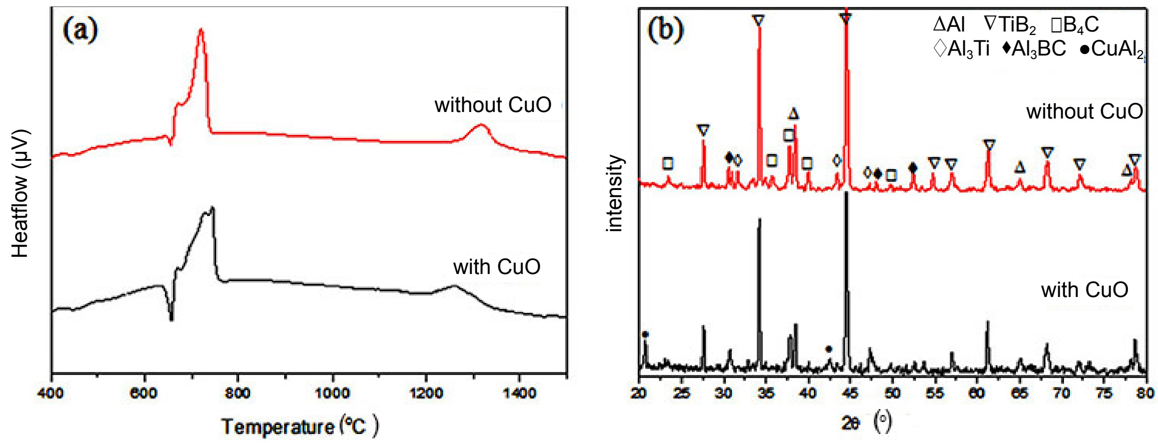


Fig. 5: (a) DTA and (b) corresponding XRD patterns of compacts with and without CuO

infiltration of the melt is involved in the DTA process. Also, the reaction environment of the QSI process is the Al melt. Compared with the QSI process, heat loss to the surroundings in the DTA process is much less.

In general, it is commonly reported that a combustion reaction can be ignited and propagated when T_{ad} >1,800 K [13]. The adiabatic temperature of the compacts with and without CuO [14] is calculated to be 1,904 K and 1,830 K, respectively. Indeed,

Table 2: Reactions in compacts

	QSI	DTA
Compact without CuO	Reaction (1) Reaction (2)(Trace)	Reactions (1) (2)
Compact with CuO	Reactions (1)(2)(3)	Reactions (1)(2)(3)

the theoretical adiabatic temperature in the CuO-free compact, 1,830 K is higher than 1,800 K, the critical temperature for a combustion reaction; which means that the combustion reaction occurs and the combustion wave can be propagated over the compact. Thus in DTA processes, the compacts both with and without CuO undergo complete reactions. However, in the QSI process, the reaction environment is the aluminum melt and also the combustion reaction and infiltration are almost simultaneous. As shown in Fig. 4(d), once the combustion reaction ignites, the temperature of the surrounding bulk aluminum melt increases immediately. It is noted that the temperature of the aluminum melt in which the CuO-free compact was involved has no obvious change as shown in Fig. 4(c). A proper explanation is that the combustion reaction in the CuO-free compact is too weak to make an obvious temperature change to the aluminum melt. However, due to the same reaction environment of the two compacts with and without CuO, it is not difficult to infer that there is also heat loss to the aluminum melt in which the CuO-free compact was involved. Owing to the heat loss to the infiltrated aluminum melt and the surrounding aluminum melt, it accordingly may decrease the compact temperature during the combustion reaction. The propagation of the combustion wave tends to be hindered and halted at a certain point and an incomplete reaction occurred in the CuO-free compact. Consequently, a wide peak temperature gap, about 330 K, is generated as shown in Fig. 4(a) and 4(b).

With the addition of CuO, the reduction of CuO with Al [reaction (3)] generates a large amount of excess exothermic heat. The reaction (3) may increase the compact temperature and also compensate for the heat loss occurring during the infiltration process. The combustion wave propagates over the compact thoroughly and a complete reaction can occur in the compact containing CuO.

It is therefore suggested that the CuO addition is effective for sustaining the combustion reaction during the QSI process.

4 Conclusion

Aluminum matrix composites with high volume fractions of reinforcing particles were manufactured successfully using a cold-compacted preform of Al-Ti-B_4C powder mixtures with small addition of CuO by the quick spontaneous infiltration method. Highly exothermic CuO reduction was employed to facilitate the complete combustion reaction of Al-Ti-B_4C in an aluminum melt. In the absence of CuO, however, combustion propagation of the Al-Ti-B_4C system was unlikely to be sustained in the aluminum melt. Accordingly, different microstructures of the composites were obtained in the compacts with and without CuO addition. In addition, the obtained composites with CuO show higher hardness, higher elastic modulus and lower CTE than that without CuO.

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