

EFFECTS OF PROCESSING TEMPERATURE ON IN-SITU REINFORCEMENT FORMATION IN Al(Zn)/Al₂O₃(ZnO) NANOCOMPOSITE

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Abstract

The aim of present work was to investigate effects of processing temperature on the microstructure of in-situ processed aluminum/alumina composites. A new activated powder injection (API) method was used to synthesize the aluminum matrix composites by displacement reaction between aluminum and zinc oxide. A mechanically activated mixture of aluminum and zinc oxide powder was injected into a vortex of molten aluminum. Three melting temperatures of 680, 730 and 790 °C were selected as the processing temperatures. The composite slurries were solidified under a pressure of 200 MPa. Microstructures of the samples were studied using electron microscopy and image analysis techniques. Refinement of in-situ reinforcements with increasing processing temperature was observed and rationalized.

Keywords: In-situ, Nanocomposite, Microstructure.

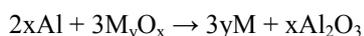
Introduction

Metal matrix composites (MMCs) are becoming more applicable because of their unique structural and mechanical properties [1-7]. Availability of inexpensive reinforcements and development of processing routes has increased the interest in MMCs for aerospace, automotive and other structural applications [8]. Aluminum alloys are widely used for the matrix of MMCs. Traditionally, aluminum matrix composites (AMCs) have been produced by processing routes like stir casting, powder metallurgy, squeeze casting, preform infiltration and spray forming [9, 10]. In such processes the reinforcing particles are added to the matrix by ex-situ method [11]. Therefore, the size of reinforcing particles is limited by the size of the starting powder particles. In addition interfacial reactions between matrix and reinforcements and poor

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wettability between the reinforcements and matrix due to surface contamination of the reinforcements are the drawbacks of ex-situ method [12]. To overcome these shortcomings in-situ method is developed in which reinforcements form in the matrix through one or more chemical reactions [13].

There are two different liquid state methods to produce in-situ aluminum/alumina composites. They are direct melt oxidation and reduction of a metallic oxide in the melt [14]. In the latter a displacement reaction occurs between aluminum and a metallic oxide. Accordingly, alumina as reinforcement and elemental metal as alloying element forms. The general reaction can be written as:



Different metallic oxides such as CuO [15-17] and SiO₂ [18] have been used to produce in-situ aluminum/alumina composites. Zinc oxide is one of the oxides which have been used for synthesizing in-situ aluminum/alumina composites. The first work, in which zinc oxide was used as the reactant metallic oxide, was published by Kobashi and Choh [19] who reported that when zinc oxide powder was added to a vortex of molten aluminum, no chemical reaction occurred. Chen and Sun [20], Yu et. al. [21], Durai et. al. [22] and Tavosi et. al. [23] also used zinc oxide as the source of oxygen to fabricate in-situ aluminum/alumina composite. The common characteristic of their works was that all of them have used aluminum powder as both the matrix and reactants. This low reactivity of zinc oxide powder with molten aluminum is attributed to very fine particle size of zinc oxide and its poor wettability by molten aluminum. Maleki et. al. [13] introduced a new activated powder injection (API) method which is capable of fabricating aluminum/alumina composite using melted aluminum ingot as the matrix when zinc oxide was used as the source of oxygen.

The main process parameters of API method are: processing (melting) temperature, reactants ratio and reactants content. The aim of the present study is to investigate effects of processing temperature, as the most critical and important process parameter, on the structure of the composites synthesized by API method.

Experimental

The materials used for matrix melt preparation were commercially pure aluminum (99.3 pct) ingot and magnesium in form of Mg-15%Al master alloy. Pure aluminum powder with particle size of less than 40 μm and pure zinc oxide powder with particle size of less than 0.5 μm were used as the reactant materials.

Aluminum/alumina composite were prepared by API method. This method consists of:

1. mechanical activation of aluminum and metallic oxide (zinc oxide in this study),
2. melt preparation and stirring,
3. injection of the activated powder deep into the melt vortex by an inert gas,
4. casting.

A mixture of aluminum and zinc oxide powders with Al:ZnO weight ratio of 2:3 were milled in a planetary ball milling machine for 60 min using hardened steel vial and balls under argon atmosphere to prevent powder oxidation. The ball to powder mass ratio was 10 and the rotation speed was 600 rpm. X-ray diffraction (XRD) analysis

performed by a Philips diffractometer (40 kV) with Cu K α radiation was conducted to detect the phases in the activated powder.

Molten Al-2.5%Mg alloy was prepared in a resistant furnace. Melting temperatures of 680, 730 and 790 °C were selected as processing temperatures. Upon reaching the desired temperature stirring started with a stirring speed of 1000 rpm. An amount of the activated powder equals to addition of 10% pure zinc oxide was injected deep into the melt using a patented injection gun with argon as the carrier gas. The composite slurries were cast in a preheated cylindrical mold, using a squeeze casting system, and solidified under a pressure of 200 MPa to avoid porosity formation. A detailed study on API method is presented elsewhere [13].

Metallographic samples were prepared according to standard methods. Hitachi S4300 field emission scanning electron microscopy (FESEM) equipped with energy dispersive X-ray spectroscopy (EDS) was used to study microstructure of the composites. Image analysis was done using Scion image software [24] to measure microstructural properties, namely average particle size, aspect ratio and particle size distribution.

Results and discussion

Aluminum and zinc oxide can react in a displacement reaction as follows [22]:



$$\Delta G_{298\text{ K}}^0 = -601 \text{ kJ/mol}$$

$$\Delta H_{298\text{ K}}^0 = -625 \text{ kJ/mol}$$

The change in free energy of this reaction is negative and therefore is thermodynamically possible, even at ambient temperature, upon providing the required activation energy. It is confirmed that the ignition temperature of this reaction is higher than 1000°C [25]. This temperature is too high for molten aluminum processing. Ball milling is capable of decreasing activation energy of the reaction and consequently its ignition temperature.

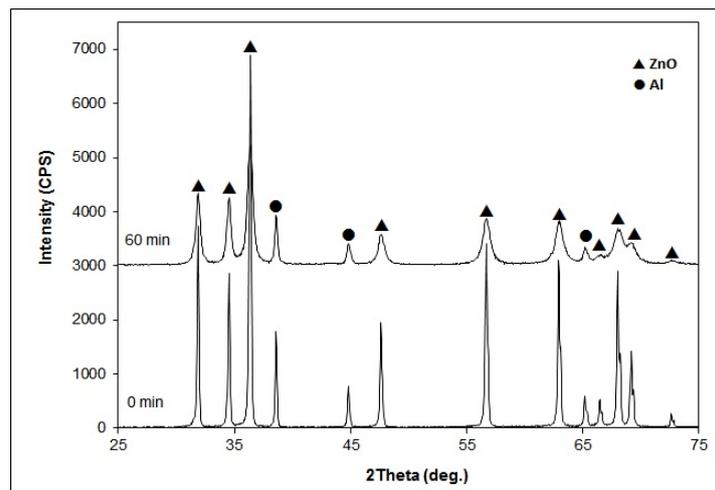


Fig.1. XRD pattern of as-mixed and 60 min activated Al-ZnO mixture

Figure 1 illustrates diffractograms of as-mixed and 60 min in planetary ball mill activated Al-ZnO mixture. It is evident that after this time of activation there is no formation of new phases. On the other hand, the aim of this process is to interact Al and ZnO powders without any displacement reaction. This decreases ignition temperature of the reaction to 563°C. A detailed study on the mechanism of abovementioned reaction is presented in reference [25].

Upon injection of the activated Al-ZnO powder deep in the aluminum melt vortex the aluminothermic reaction ignited and alumina as in-situ reinforcement and zinc as in-situ alloying element were dispersed in the melt. It is noticeable there is no excess aluminum powder to be dissolved in the melt, because Al:ZnO ratio in the activated powder is close to stoichiometric. Figure 2 illustrates the microstructure of slurries prepared at temperatures of 680, 730 and 790°C and solidified under pressure using squeeze casting system. As can be seen that reinforcing particles were distributed in the matrix. It confirms successfulness of the in-situ process and entrapment of alumina particles in matrix.

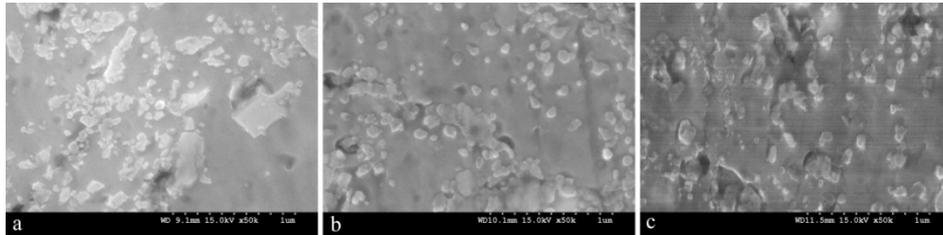


Fig. 2. SEM micrograph of Al(Zn)/Al₂O₃(ZnO) composites processed at a) 680, b) 730 and c) 790 °C

Average diameter for largest and smallest dimension of reinforcement particles at each temperature was measured and presented in Figure 3.

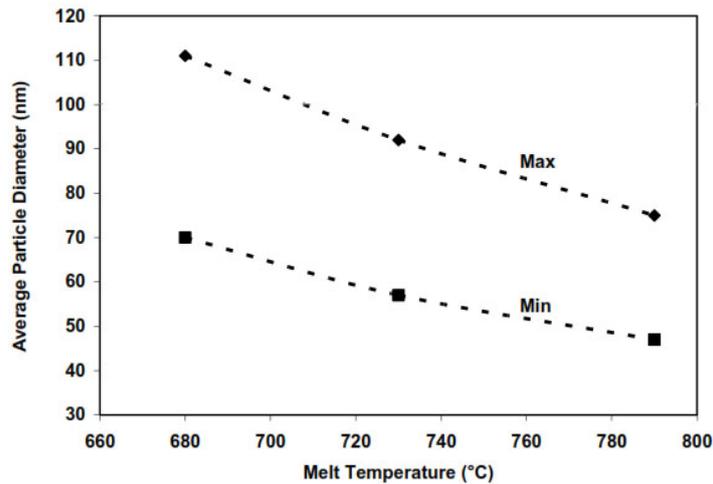


Fig. 3. Average of minimum and maximum diameter of reinforcement particles in Al(Zn)/Al₂O₃(ZnO) composites processed at 680, 730 and 790 °C

It is evident that as the melting temperature increases average alumina particles size decreases. Average aspect ratio of reinforcement particles was measured to be 1.63, 1.65 and 1.62 for temperatures of 680, 730 and 790 °C, respectively. It means there is no meaningful difference in the aspect ratio or, in the other word, roundness of reinforcing particles at different synthesizing temperatures.

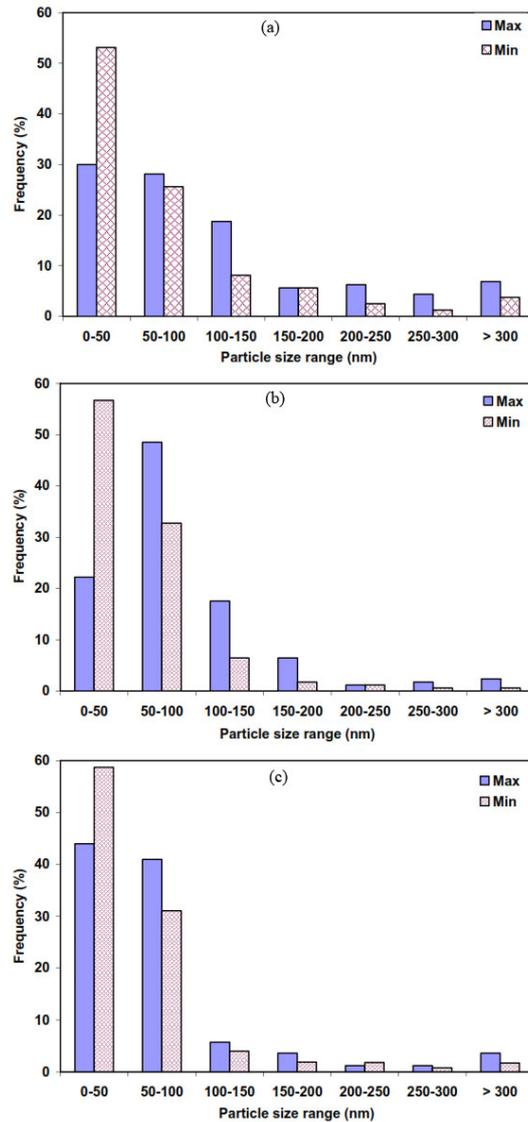


Fig. 4. Reinforcement particles size distribution in Al(Zn)/Al₂O₃(ZnO) composites processed at a) 680, b) 730 and c) 790 °C

In Figure 4 distribution of particle size in certain ranges is shown. It can be seen that size of majority of reinforcements is below 100 nm.

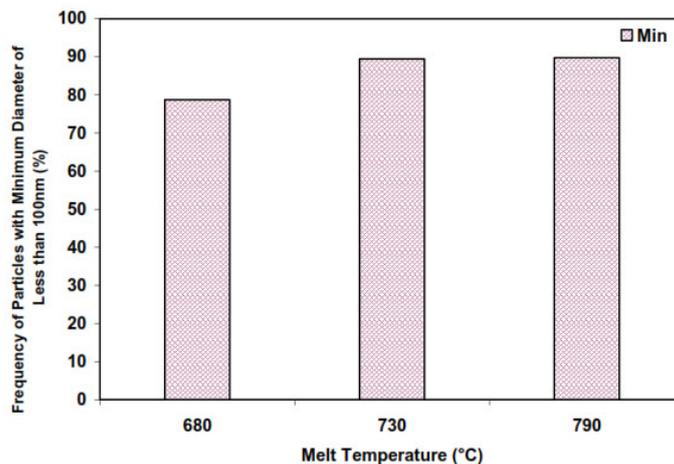


Fig. 5. Percentage of reinforcement particles smaller than 100 nm in Al(Zn)/Al₂O₃(ZnO) composites processed at 680, 730 and 790 °C

Figure 5 quantifies this fact. From Figures 3 and 5 it is evident that average size of particles decreases by increasing melting temperature. However, there is small change in percentage of particles lesser than 100 nm and particularly at melting temperature above 730°C where is a negligible change. For processing temperature of 680°C, almost 80 percent of particles are lesser than 100 nm, while this amount increases at 730 and 790°C processing temperature and reaches 90 percent.

These measurements show refinement of reinforcing particles with increasing processing temperature. This refinement can be explained based on the proposed mechanism of reinforcement formation in activated powder injection method as follows.

Figure 6 indicates activated particles of Al-ZnO. In formation of alumina in melt each Al-ZnO particle reacts independently. On the other hand, since addition of activated powder to melt is gradual, in such a way that melting temperature is roughly constant, its exothermic reaction has no thermal effect on the reaction of other particles. The stages in formation of alumina are:

- 1- entrance of activated powder into melt with carrier gas,
- 2- heating of powder particle to ignition temperature by the melt,
- 3- aluminothermic reaction and formation of alumina and zinc vapor,
- 4- fragmentation and dispersion of alumina particles in consequence of explosion caused by the reaction.

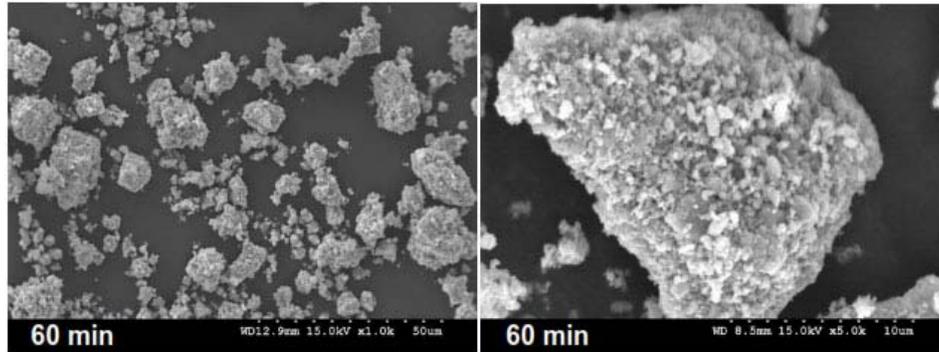


Fig. 6. SEM micrograph of 60 min activated Al-ZnO mixture in two magnifications

At high temperatures aluminothermic reactions are explosive [17], i.e. the reaction rate is very high [20]. If the activated powders are assumed to be ignited at aluminum melting temperature, i.e. 660°C, its rate constant (k), which is a scale to evaluate reaction rate [26], is of order 106 for aluminum and zinc oxide reaction, i.e.:

$$k = A \cdot \exp(-Q/RT)$$

Where A is a pre-exponential factor, Q is the activation energy, R is the universal gas constant and T is temperature.

This high value of rate constant confirms that the reaction can be considered explosive. At the same time the adiabatic temperature of the reaction is as high as the reduced zinc is in form of gas (vapor). The high reaction rate and simultaneous gas formation can induce micro scale explosion, fragmentation and dispersion of alumina particles.

Alumina particles are very fine because of the following argument. Zinc oxide particles are inherently submicron and compared to aluminum powder particles are very small. Therefore, each Al-ZnO particle consists of many ZnO particles embedded in an aluminum powder particle (Figure 6). After ball milling, each Al-ZnO composite particle can be assumed as less than 50 micron reactor, as shown in Figure 6 (right). Because of small size of the reactors and high ambient temperature (molten aluminum) all ZnO particles react simultaneously at high rate. In fact, the reaction mechanism changes from surface reaction to volume reaction because of high reaction temperature and rate [27]. When exothermic reaction is explosive it can be considered adiabatic [17]. In this condition all the released heat is consumed for heating of products and, consequently, the products expand suddenly. For brittle particles this sudden expanding can cause fragmentation. The explosion energy also promotes refinement of reinforcing alumina particles.

It should be noted that products size depends on reactants size [28]. Considering this fact, the very fine particle size of zinc oxide is another cause for formation of small alumina particles. However, there are some particles noticeably bigger than the average size. If in the abovementioned reactor some zinc oxide particles become very close or agglomerates, they can form these larger alumina particles.

Considering the alumina formation mechanism, refinement of alumina particles with melting temperature increase can be also explained.

Figure 7 shows a model for the assumed reactor. The reaction in the reactor can be propagating or simultaneous combustion. For this reactor Biot number is of order 10^6 , therefore its temperature is homogeneous and its reaction is of simultaneous combustion type.

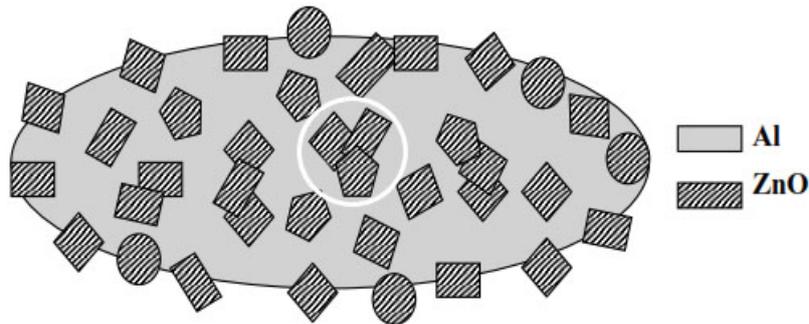


Fig. 7. Schematic model for activated Al-ZnO mixture

When melting temperature, or the temperature of reaction ambient, increases, reaction rate constant (k), and consequently reaction rate or explosion intensity of the reaction, increase as well. Reaction rate is:

$$d\alpha/dt = k \cdot f(\alpha)$$

where α is the fraction reacted, t is time (min), k is a rate constant (min^{-1}) and $f(\alpha)$ is a particular kinetics function whose form should be defined based on the reaction mechanism.

On the other side, adiabatic temperature, i.e. products temperature also increases. At reaction explosion flash, zinc vapor can be considered as an ideal gas [29]. It means PV/T is constant where P is pressure of zinc vapor, V is volume of zinc vapor and T is its temperature which is equal to adiabatic temperature. When melting temperature increases adiabatic temperature, and consequently PV , also increases. In addition, when melting temperature increases, the energy of the gas (zinc vapor) increases. At the same time the strength of the reinforcing particles decreases because of higher temperature. It means that with increasing melting temperature particles with lower strength tolerate higher force and therefore become finer.

Conclusion

In activated powder injection method increasing processing temperature decreases the average particle size of reinforcement. This is because of:

- explosive reaction of Al-ZnO composite particles,
- gas formation during aluminothermic reaction of Al and ZnO,
- sudden expansion of products of Al-ZnO reaction,
- increased energy release of Al-ZnO reaction by increasing melting temperature.

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