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# Producing ternary intermetallic compounds powders by solid–liquid reaction ball milling

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**Abstract** A novel mechanochemistry approach, defined as solid–liquid reaction ball milling, was applied to obtain single-phase Al–Cu–X (X = Fe, Co, and Ni) ternary intermetallic compound powders by reactions between milling medium (ball and cylinder) and liquid-state metals in certain temperature range, where the milling mediums made of metals with high-melting point and took part in the reaction as the solid-state reactants. Compared with the conventional mechanical milling technique, nanometer-sized intermetallic compound powders and some single-phase ternary intermetallic phases could be obtained at lower temperatures by the solid-state reaction ball milling. Furthermore, the reaction mechanisms of this mechanochemical approach have been discussed in details.

## Introduction

Intermetallic compound is a sort of the metallic materials that attracted intense interest by material scientists and engineers, and its ordered nature leads to attractive elevated temperature properties such as high strength, increased stiffness, and excellent corrosion/oxidation resistance. However, the low-ambient temperature ductility and fracture toughness preclude large-scale industrial applications of intermetallic compounds. The ball milling/mechanical alloying process has been verified to be a successful approach to improve the room-temperature ductility of intermetallics in the past several decades, because it can reduce grain size, disorder lattice and modify crystal structure of the phase into a more symmetric one [1–4]. Thus, mechanochemistry approach (reaction milling) became an important route to obtain high-performance intermetallic compound powders [5–8].

Although the chemical reactions of intermetallic synthesis caused by solid–solid and solid–gas reaction are very common, the investigations and reports on solid–liquid reaction are extremely limited [7, 8]. The most possible reason is that almost all metals (except for Hg) and alloys are solid state at room temperature, and the effects of external fields such as magnetic field, the electric field, and ultrasonic field, on the solidification behavior of metal melts have attracted much attention in the past half century [9, 10]. Considering milling a melt, the portion of melt in direct contact with the balls involves high pressure and enhances atomic reactivity, which can induce solid–liquid mechanochemical reactions. It has been recognized that this kind of reactions can occur at room temperature or lower temperature than those normally required for the preparation of pure metal particles, nanocomposite powders and other useful functional materials in the material chemistry and relative fields [11]. However, there is still much more work required for the synthesis of high-purity intermetallic compounds by means of the solid–liquid mechanochemistry reaction route.

Recently, a novel solid–liquid reaction ball milling technique based on the coupling effect of both mechanochemistry and thermochemistry was developed by our group [12–16]. Many types of binary intermetallic compound powders were fabricated successfully and most of them are single-phase nanoparticles. Compared with traditional mechanical alloying (MA, i.e., high energy ball milling) processes, this mechanochemistry approach shows the advantages in finer particle size, higher purity of production, faster reactivity speed and different microreaction mechanism. In this present study, a number of ternary intermetallics of Al–Cu–X (X = Fe, Co, Ni) alloy systems

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such as $Al_7Cu_2Fe$, $Al_{13}Cu_4Fe_3$, $Al_{65}Cu_{20}Fe_{15}$, $Al_{65}Co_{15}Cu_{20}$, $Al_{69}Co_{25}Cu_6$, $Al_{17}Cu_4Ni$, and $Al_{0.28}Cu_{0.69}Ni$ have been successfully prepared.

## Experimental equipment and process

The solid–liquid ball milling equipment developed by the authors were shown in author's previous reports [5, 13], in which a sealed milling cylinder of 300 mm in diameter rotates in a resistance-heated furnace equipped with the thermostatic system. Both the balls and the milling cylinder (or inner liner of the milling cylinder) are made of the same starting materials to avoid the melt from contamination.

The milling cylinder was vacuumed first and then filled with pure inert gas to avoid oxidation of the metals during milling at the chosen temperatures. Metal with high-melting point is termed as the starting materials, while the metal with low-melting point is termed as the reactants. The weight ratio of the balls to the reactant was 20:1 to 30:1 for different alloy systems. The rotation speed was kept at 80 rpm. It must be pointed out that the balls need to be replaced timely during the milling process. The milling temperature was chosen to be about 50 °C higher than the melting point of the reactant to make sure that the reactants were in molten state during the milling process.

In this system, the Fe, Co, and Ni of balls and the milling cylinder acted as the starting materials. Different binary alloy ingots, i.e., Al–33.2 wt% Cu, Al–54 wt% Cu, Al–70 wt% Cu, were served as the reactants. The as-milled products were examined by X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM).

## Results

The ternary intermetallic compounds powders obtained by the solid–liquid reaction ball milling were shown in Table 1. It can be seen that a number of single ternary Al–Cu–Fe alloys powders were obtained after milling the Al–33.2 wt% Cu melts for 48 h. $Al_7Cu_2Fe$ was prepared after milling for 12 h when 20 wt% iron powders was added into the melt. $Al_{13}Cu_4Fe_3$ and $Al_{65}Cu_{20}Fe_{15}$ phases were obtained after milling the Al–45 wt%Cu melt blended with 20 wt% iron powders at 943 K for 12 h and 48 h, respectively. Obviously, the iron powders accelerated the reaction rate.

Similar to the Al–Cu–Fe system, $Al_{65}Cu_{20}Co_{15}$ and $Al_{69}Cu_6Co_{25}$ ternary intermetallic compound phase of Al–Co–Cu systems and $Al_7Cu_4Ni$ and $Al_{0.28}Cu_{0.69}Ni_{0.02}$ ternary intermetallic compound phase of Al–Cu–Ni systems have been obtained by this solid–liquid reaction ball milling technology, respectively. However, with increasing of the milling temperature and the content of Cu/Ni in the reactants, the formation of the ternary alloy phases became difficult. The XRD patterns of Al–Cu–X (X = Co, Ni) ternary intermetallic powders are given in Fig. 1, which shows that some single ternary intermetallic phase, i.e., $Al_{69}Cu_6Co_{25}$, $Al_{65}Cu_{20}Co_{15}$, and $Al_{0.69}Cu_{0.28}Ni_{0.02}$ were obtained by the mechanochemistry approach.

The TEM images of the as-milled products of the Al–Cu–X (X = Fe, Co, and Ni) intermetallic compound powders are shown in Fig. 2, which demonstrates that these intermetallic powders are composed of agglomerated particles with an average size of <100 nm.

## Discussions

Traditionally, ternary alloy phases are prepared by ingot metallurgy technology, which requires a high-temperature processing or powder metallurgy processing. In fact, the powder metallurgy processing also requires high temperature or complex sintering processing. However, during the present solid–liquid reaction milling process, pure intermetallics phase powders such as $Al_{13}Cu_4Fe_3$, $Al_{69}Cu_6Co_{25}$, and $Al_{0.28}Cu_{0.69}Ni_{0.02}$ were successfully prepared at temperatures much lower than their melting points. In addition,

**Table 1** The as-milled products of Al–Si–Fe and Al–Cu–Fe system obtained by solid–liquid reaction milling

| System | Reactants | *T* (K) | Phase constituents of the as-milled products (h) | | |
|---|---|---|---|---|---|
| | | | 12 | 24 | 48 |
| Al–Cul–Fe | Al–33.2 wt% Cu | 923 | $Al_7Cu_2Fe$, a little $Al_2Cu$ | $Al_7Cu_2Fe$, $Al_{13}Cu_4Fe_3$ | $Al_{13}Cu_4Fe_3$ |
| | Al–54 wt% Cu | 943 | $Al_{13}Cu_4Fe_3$, a little $Al_2Cu$ | $Al_{13}Cu_4Fe_3$, $Al_{65}Cu_{20}Fe_{15}$ | $Al_{65}Cu_{20}Fe_{15}$ |
| Al–Cul–Co | Al–33.2 mass% Cu | 893 | $Al_{65}Cu_{20}Co_{15}$ | $Al_{69}Cu_6Co_{25}$ | – |
| | Al–54 mass% Cu | 993 | $Al_{65}Cu_{20}Co_{15}$ | $Al_{65}Cu_{20}Co_{15}$ | – |
| | Al–70 mass% Cu | 1123 | No ternary alloy | $Al_{65}Cu_{20}Co_{15}$ | – |
| Al–Cul–Ni | Al–33.2 mass% Cu | 893 | $Al_7Cu_4Ni$,$Al_4Cu_9$ | $Al_7Cu_4Ni$,$Al_4Cu_9$ | – |
| | Al–54 mass% Cu | 993 | No ternary alloy | $Al_{0.69}Cu_{0.28}Ni_{0.02}$ | – |
| | Al–70 mass% Cu | 893 | No ternary alloy | $Al_{0.69}Cu_{0.28}Ni_{0.02}$, $Al_4Cu_9$ | $Al_{0.69}Cu_{0.28}Ni_{0.02}$ |

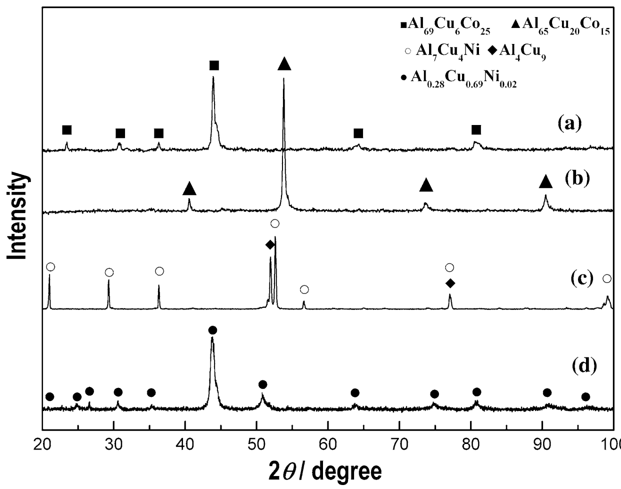



**Fig. 1** X-ray pattern of Al–Cu–X (X = Co, Ni) system ternary intermetallic powders which were obtained by solid–liquid reaction. **a** and **b** were obtained at 923 K by milling Al–33.2 mass% Cu melting with Co mill medium for 12 and 24 h, respectively. **c** and **d** were obtained at 893 K by milling Al–33.2%Cu and Al–54%Cu melting with Ni mill medium for 24 h, respectively

although some ternary alloy powders, such as $Al_{65}Cu_{20}Co_{15}$, obtained in this present work could also be obtained by using the high-energy planetary ball mill technology in recently years [17]. Some other ternary intermetallic compound phases (such as $Al_{69}Cu_6Co_{25}$, $Al_7Cu_4Ni$, and $Al_{0.28}Cu_{0.69}Ni_{0.02}$) obtained in the present work are hard to be prepared directly by the general mechanical alloying process according the existed literatures.

## Reaction mechanism of solid–liquid reaction milling ball process

During the mechanochemical process, ball milling can cause crystal lattice distortions, crystal defects, and electron emission, resulting in great chemical activity improvement and reaction rate increase. Thereby, the activity of the starting material, iron here, is high enough to accelerate the reaction and shorten the milling time for the formation of pure intermetallics. Additionally, the collisions among the milling balls lead the temperatures rise above the melting point of the ternary alloy, which are benefits to its formation. Moreover, the final ternary alloy products are characteristic of the same elemental molar ratio as the original binary alloy.

One characteristic of this novel solid–liquid reaction milling technique is that nanometer-sized intermetallic particles can be prepared. The formation mechanism can be explained as the followings: during this process, the newly formed reaction products on the surface of the balls peels off and breaks into fine particles during the continuous collisions between the balls. The fresh surface helps to accelerate the solid–liquid reaction rate to form the intermetallics layer. This kind of cycles will not stop until the melt is totally consumed out. The added metal powders provide more reaction surface area to further accelerate the reaction rate. The as-formed particles deposit in the melt in solid state. Further, these nanometer-sized powders will not readily vanish or grow up by continuously impacts during ball milling.

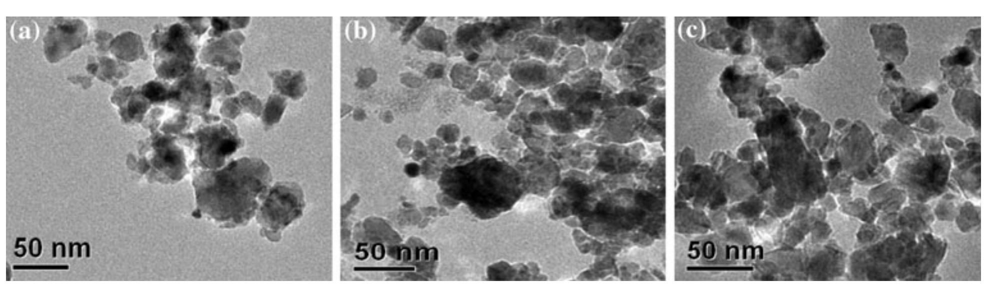
## The comparisons of solid–liquid reaction ball milling with the commonly used mechanical alloying

Reaction milling process has advantages over the conventional mechanical alloying such as high-energy ball milling and tumbler milling. The former involves a direct reaction, while the latter involves repeated flattening, cold welding, fracturing, rewelding, and solid-state diffusion processes at atomic scale of powders. Consequently, solid–liquid reaction ball milling processing possess higher reaction rate than that of the mechanical alloying processing. Furthermore, when the alloy systems are treated by high-energy ball milling, amorphous phase rather than intermetallics can be obtained in most cases after milling for a long time [5, 18, 19].

The advantages of the mechanochemistry approach compared with the commonly mechanical alloying process can be summarized as follows:

(1) In the solid–liquid reaction ball milling process, the reaction activation energy is significantly decreased, which could produce some alloys and compounds that cannot be obtained by the mechanical alloying process.

**Fig. 2** TEM images of ternary alloy powders obtained by solid–liquid reaction ball milling. **a** Al–Cu–Fe, **b** Al–Cu–Co and **c** Al–Cu–Ni



(2) The ternary intermetallics compound powders are produced by solid–liquid reaction from the beginning of the ball milling process, which means no induction period of solid–liquid reaction in this process. The following process is only the accumulation of the reaction products until the liquid melts is fully exhausted. However, during the mechanical alloying, the chemical reaction process has an induction period, which is a period of accumulation of the reaction energy. Then, the mechanical alloying begins and intermetallic compound powders formed.
(3) The products of the mechanochemistry approach are in nanometer size, because of the small area of the solid–liquid reaction and the continuous ball milling impacting effects. One feature of the common mechanical alloying is producing ultrafine powders, and most of the powders are nanocrystalline powders. However, nanometer-sized powders are difficult to be produced directly through solid-state mechanical alloying.
(4) The products of the mechanochemistry approach and the mechanical alloying are not completely the same. In this study, the products of Al–Cu–Fe systems are ternary intermetallic powders. However, the products of the mechanical alloying are usually amorphous and oversaturated solid solution powders, the intermetallic compound phases were not obtained [19].

## Summary

A series of Al–Cu–X (X = Fe, Co, and Ni) ternary intermetallic powders, such as $Al_7Cu_2Fe$, $Al_{13}Cu_4Fe_3$, $Al_{65}Cu_{20}Fe_{15}$, $Al_{65}Co_{15}Cu_{20}$, $Al_{69}Co_{25}Cu_6$, $Al_{17}Cu_4Ni$, and $Al_{0.28}Cu_{0.69}Ni$, have been successfully prepared by solid–liquid reaction milling. Most of the products are in single phase. As a new intermetallic compound powder preparation approach, solid–liquid reaction ball milling shows some promising applications to extend the industrial-scale applications of intermetallic compounds. The formation mechanism of the solid–liquid reaction milling has different reaction mechanism with the common mechanical alloying process.

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