Reduction reaction in Al-CuO powder mixture driven by mechanical alloying[①]

Wu Jinming(吴进明), Zheng Shilie(郑史烈), Li Zhizhang(李志章), Wu Nianqiang(吴年强)

Department of Materials Science and Engineering,

Zhejiang University, Hangzhou 310027, P.R.China

Abstract: The solid state reduction reaction of Al-10％CuO mixed powders during mechanical alloying was investigated using XRD, DTA and TEM. The CuO is believed to be gradually reduced by Al, and controlled by diffusion of atoms and ions. Reduced Cu spontaneously reacts with Al to form a metastable equilibrium of Al (Cu) with Al_4Cu_9 phase during ball-milling, instead of $CuAl_2$ and Al(Cu), which is only observed after annealing.

Key words: solid state reaction; mechanical alloying; phase transformation   **Document code:** A

1 INTRODUCTION

Nano-sized particles reinforced metal matrix composites[1,2] and nano-sized elemental metal particles[3~5] can be obtained by certain reactions during ball-milling which are difficult to occur under conventional conditions. The mechanically driven reduction reaction of CuO (or Cu_2O) + M $\rightarrow$ Cu + M_xO_y (M = Al, Ca, Mn, Ti, Fe, Ni, etc.) has been applied to produce nano-sized Cu particles. However, the mechanism of the displacement reaction process has not been well understood. In Schaffer's opinion, local reaction is believed to occur spontaneously when the reactants are brought into atomic contact. When the rate of heat generating by the local reaction is greater than that of heat dissipation, the reaction is completed through a process similar to the thermal ignited combustion[4,5]. However, Sherif et al found that the product coexists with reactants within a long ball-milling period. This indicates that the reaction proceeds in a diffusion-controlled manner, and the oxide is gradually reduced during ball-milling[3]. To further understand the mechanism, the reduction reaction of Al-10％ CuO mixed powders during high energy ball milling is investigated in this paper.

One of the reasons to select the Al-CuO system relies on the possibility to achieve particle reinforced Al_2O_3/Al-Cu composites.

2 EXPERIMENTAL

The Al (purity 99.0％, 74 μm) and CuO (purity 99.0％, 74 μm) powders were mixed to give the nominal composition of Al-10％ CuO. Ball milling of powder mixture was performed in a QM-1SP planetary ball-mill under Ar atmosphere using a hardened steel vial and 450 g of steel balls (10 mm in diameter). The planetary rotation speed was 230 r/min and mass ratio of the ball to the powder was 30：1. About 1％ of stearic acid was added to prevent the agglomeration of the powders. At selected time, a small amount of the as-milled powders were taken for analysis.

The mixed powders were characterized using a Rigaku D/max-3B X-ray diffractometer with CuKα radiation, λ = 0.154 18 nm, and a JEM-100CX transmission electron microscope. Differential thermal analysis (DTA) was carried out to investigate temperature induced reaction and/or phase transformation of the as-milled powders using Perkin-Elemer DTA1700 instrument at a heating rate of 10 K/min.

3 RESULTS

3.1 Reaction of Al-10% CuO powder mixture during ball-milling

The XRD patterns of the Al-10 % CuO powder milled for different times are presented in Fig. 1. It can be seen that the intensities of CuO peaks decreased with increasing milling time (as illustrated in Fig. 1(a), (b)). After 15 h of milling, the CuO peaks vanished and only the Al peaks were detected (Fig. 1(c)). With increasing the milling time to 17 h, new peaks corresponding to Al_4Cu_9 appeared (Fig. 1(d)), and its intensities increased on further milling to 56 h (Fig. 1(e)). The peaks corresponding to Al_2O_3 failed to be detected in all related XRD patterns. This was probably due to its low concentration of about 3%. No changes were found on further milling to 115 h.
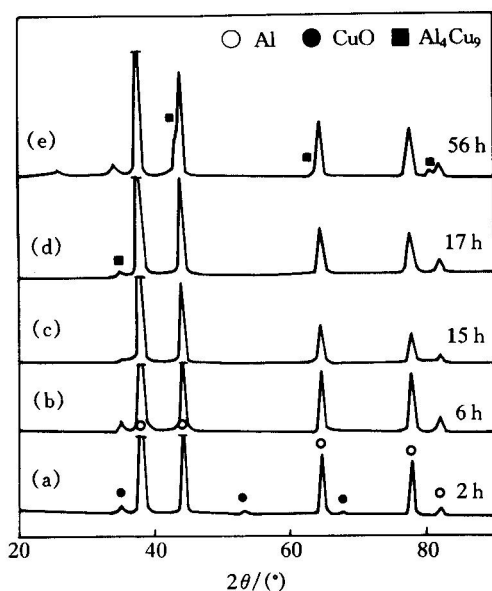

Fig.1 XRD patterns of Al-10% CuO mixed powders after different milling times

Fig. 2 shows the DTA curves for the Al-10%CuO as-mixed powders (a) as well as the powder mixture after (b) 2 h, (c) 6 h, (d) 15 h, (e) 47 h of ball-milling. All the samples were heated to 870 ℃ in Ar atmosphere. Sharp endothermic peaks at about 640 ℃ appeared in

Fig. 2 due to melt of the metallic Al. The reduction reaction did not occur up to 870 ℃ in as-mixed powders, as showed in Fig. 2(a). However, after ball-milling, heating induced reaction of the two reactants (CuO and Al), which is characterized by an exothermic peak occurred at about 200～330 ℃ (as displayed in Fig. 2(b)～(d)). The reaction temperature was about 330 ℃ after 2 h of ball-milling, and decreased to about 200 ℃ after 4 h of further ball-milling. After 47 h of ball-milling, a sharp endothermic peak corresponding to the eutectic reaction in Al-Cu binary phase diagram appeared at about 544 ℃ (as displayed in Fig. 2(e)). No trace of the CuO + Al reaction was detected in Fig. 2(e), suggesting completion of the reduction reaction after 47 h of ball-milling.
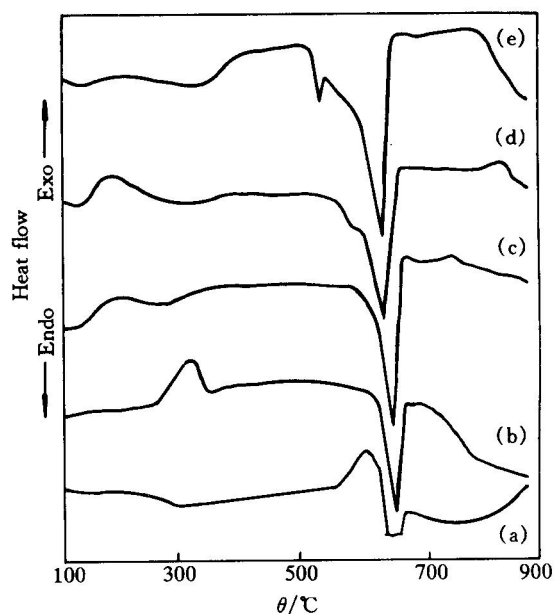

Fig.2 DTA curves for CuO milled with Al after certain milling times
(a)—0 h; (b)—2 h; (c)—6 h; (d)—15 h;(e)—47 h

As mentioned above, only the Al peaks exist in the XRD pattern of the powder mixture after ball-milled for 15 h. The similar XRD pattern has been obtained by Xi et al, who ball-milled Al-15% CuO and Al-30% CuO mixed powders. They stated that CuO has been reduced by Al to

form Al(Cu) + Al$_2$O$_3$ mixed powders[6]. However-
er, it is clear from the exothermic peak in Fig.2
(c) that the reduction reaction between CuO and
Al did not occur completely. To observe the
morphology of CuO after ball-milled for 15 h,
TEM observation has been performed and the re-
sult is showed in Fig.3. It can be seen that CuO
particles with size of 10~50 nm dispersed in the
Al matrix, which were also surrounded by lots of
defects. Thus, we suggested that the absence of
the CuO peaks may be attributed to the refine-
ment of CuO to nano-size, the severe deforma-
tion of the lattice of CuO and perhaps a
metastable structure of Cu···O···Al with weak
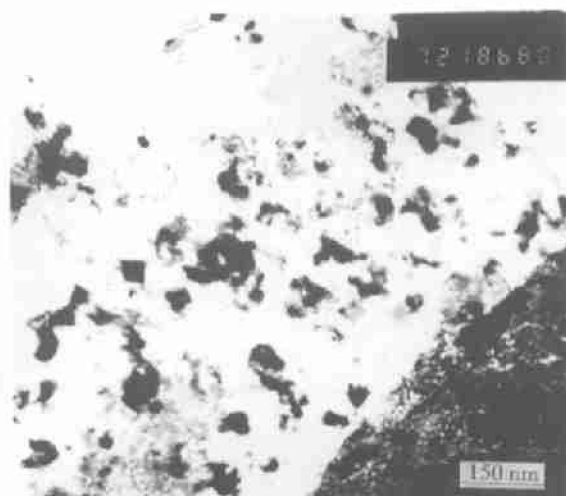bonds between each atoms developed during ball-
milling.

Fig.3   Morphology of Al-10%CuO
powder mixture after ball-milled for 15 h

3.2   Effect of temperature on reaction of Al-10%CuO mixed powder

Fig.4 and Fig.5 give the XRD patterns of
the Al-10%CuO mixed powders after ball-milled
for different time and followed by vacuum heat-
ing at (a) 250℃, (b) 400℃ and (c) 600℃,
respectively for 1.5 h. A summary of the reac-
tions observed is given in Table 1. The XRD
patterns of the powder mixture after 20 h of ball-
milling is similar to those shown in Fig.1(e).

As showed in Table 1, the reduction reac-
tion induced by heating was different from that

by ball-milling. Heating below the eutectic reac-
tion temperature (548℃), the metallic Cu re-
duced by thermal activated process coexisted
with Al. Some intermediate Cu$_2$O phases were
also present (see Fig.4(b)). However, on ball-
milling, the metallic Cu produced by mechani-
cally driven process was alloyed with Al to
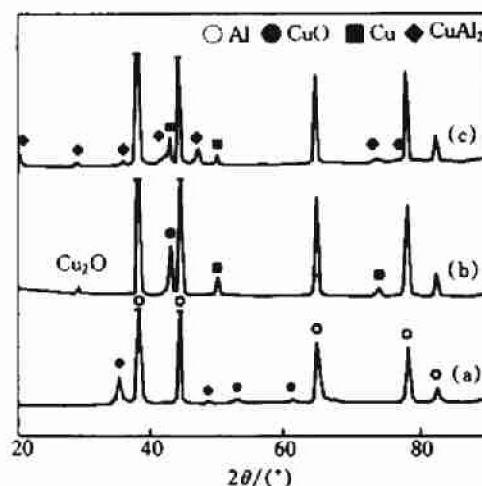form the Al$_4$Cu$_9$ intermetallic, which trans-

Fig.4   XRD patterns of Al-10% CuO mixed
powders after ball-milled for 2 h and
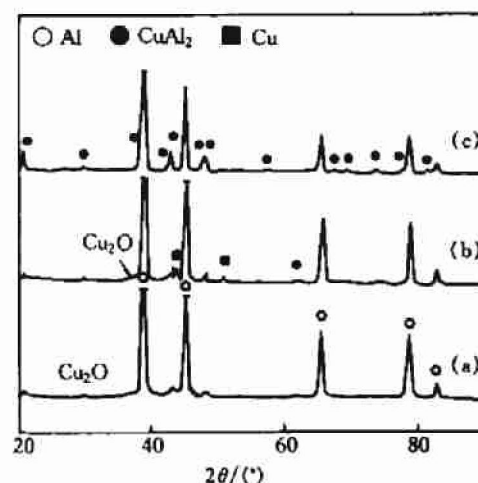heated at different temperatures
(a)—250℃; (b)—400℃;(c)—600℃

Fig.5   XRD patterns of Al-10% CuO mixed
powders after ball-milled for 20 h and
heated at different temperatures
(a)—250℃; (b)—400℃; (c)—600℃

Table 1 Phases observed in Al-10%CuO mixed powders after ball-milled and followed by heating

	MA	250 ℃	400 ℃	600 ℃
0 h	—	Al + CuO	Al + CuO	Al + CuO
2 h	Al + CuO	Al + CuO	Al + Cu + Cu$_2$O*	Al + Cu + CuAl$_2$ + Cu$_2$O*
20 h	Al + Al$_4$Cu$_9$	Al + CuAl$_2$ + Cu* + Cu$_2$O*	Al + CuAl$_2$ + Cu* + Cu$_2$O*	Al + CuAl$_2$

* Referring to the trace phase. The probably produced Al$_2$O$_3$ phase is not illustrated.

formed to the equilibrium CuAl$_2$ phase during heating. The presence of Cu and Cu$_2$O in the mixed powders after ball-milled for 20 h and heated at 250 ℃ and 400 ℃ indicated that the reaction did not finish, although no peak corresponding to the reactant CuO was detected after 15 h of ball-milling.

4 DISCUSSION

4.1 Reduction reaction of CuO with Al

As described previously, the reduction reaction of CuO with Al will not occur until heating to 1 273 K. Although the surface-active element such as Mg is added to reduce the reaction temperature, it is still higher than the melting point of Al[7]. In this experiment , the reaction temperature of CuO with Al has been successfully reduced to 330 ℃ after 2 h of milling, and further decreases with prolonged milling. It is evident in Fig. 4 that CuO reacts with the Al completely when the Al-10%CuO mixed powders milled for 2 h is heated at 400 ℃ .

Considering the phase evolution of the Al-10%CuO mixed powders (Fig. 1), the following reaction process can be suggested: 2Al + 3CuO→ 3Cu⋯3O⋯2Al→3Cu + Al$_2$O$_3$. At the initial stage of ball-milling, CuO particles are dispersed in the Al matrix and are refined to 10～50 nm by further milling (Fig. 3), with increasing the contact area of the CuO and Al reactants. Large quantities of grain boundaries induced by ball-milling and defects in the boundary of CuO and Al provide short-circuit diffusion paths for the atoms or ions either. The product layers and the reactants are separated dynamically, minimizing the deterioration effects of product barriers. Thus, the activation energy and the reaction temperature are lowered. Once lowered reaction temperature is low enough to reach the local

temperature induced by ball-milling, generally estimated to be 300 ～ 600 ℃[8], the reduction reaction occurs. The peaks corresponding to the reduced Cu did not appear in the XRD patterns because of the immediate alloying of Cu with Al to form a metastable phase Al$_4$Cu$_9$, which will be discussed in paragraph 4.2.

Previous investigation suggested that a combustion reaction occurs in the mixed CuO and Al powders with stoichiometry[4]. However, in the present work, the rate of reaction at the local area is greatly retarded due to dilution of the reactants of the excessive Al. As seen in the DTA curve (Fig. 2 (d)), the reduction reaction has not initiated after 15 h of ball-milling, though no peak corresponding to CuO can be detected in the XRD pattern (Fig. 1). After 17 h of ball-milling, the Al$_4$Cu$_9$ peaks appear and the intensities of the peaks increase during subsequent ball-milling. In addition, after milled for 20 h the mixed powders are subsequently heated at 250 ℃ and 400 ℃ , some Cu and Cu$_2$O will be formed. So it is clear that the reduction reaction starts after 15 h of ball-milling and does not complete till 20 h of milling. The fact that combustion reaction is restrained by dilution of inert component has also been found in the Ti-Al-C mixed powders under the same ball-milling conditions. The TiC has been formed gradually due to the existence of Al[9].

As seen in the Al-Cu binary phase diagram, the CuAl$_2$ phase or other intermetallic can be achieved only by heating the elements Al and Cu up to 548 ℃ , so it is not surprising that the metallic Al, Cu and minor Cu$_2$O are obtained after the Al-10% CuO mixed powders ball-milled for 2 h and heated at 400 ℃ . The presence of Cu$_2$O is an evidence that the CuO is reduced by Al via the following route: CuO → Cu$_2$O →

$Cu^{[10]}$. Being heated below 548 ℃, $CuAl_2$ phase must be transformed from the metastable Al_4Cu_9 produced during ball-milling. Therefore, the reaction is believed to occur after 20h of ball-milling and gradually complete on further milling to 47 h. This fact is supported by the remarkable endothermic peak in Fig.2(e).

4.2 Formation of metastable Al_4Cu_9 phase

The end products of ball-milled Al-10% CuO mixed powders are composed of Al, Al_2O_3 and Al_4Cu_9. The metallic Cu reduced from CuO is alloyed with Al to form a metastable Al_4Cu_9 phase.

According to Al-Cu binary phase diagram, the free energy of the three related phases FCC $\alpha(Al)$, γ-Al_4Cu_9 and θ-$CuAl_2$ at 300 K is schematically illustrated in Fig.6. The free energy values at point A, B and C were calculated on the basis of the thermodynamic data provided by Muray[11]. According to the common tangent rule, the free energy of the system consisting of Al(Cu) + θ and Al(Cu) + γ fixes on the line AB and AC, respectively. Let ΔG be the different of free energy between the equilibrium θ phase and γ metastable phase, it is estimated from Fig.6 that the value of ΔG is 0.5 kJ/mol for Al-10%CuO (Al-3.5% Cu (mole fraction)). The maximum excessive free energy induced by ball-milling is defined as ΔG_{MA}, it is believed that the metastable phase is achieved if the condition of $\Delta G_{MA} > \Delta G$ is attained[12]. Many factors may contribute to ΔG_{MA} during ball-milling. Although the value of ΔG_{MA} due to defects and strain energies during ball-milling are negligible[12], the refinements of the grain size (d) to about 20 $nm^{[13]}$ during alloying corresponds to a maximum increase in the grain boundary enthalpy of the alloy of $\Delta G = 3\sigma_{gb} V_m/d = 0.75$ kJ/mol, where $V_m = 10.0$ $\mu m^3/mol^{[14]}$ is the mole volume of Al, and σ_{gb}, the grain-boundary enthalpy, is estimated to be 0.5 $J/m^{[15]}$. Therefore, according to thermodynamic, it is possible that the Al_4Cu_9 phase is formed in the Al-10% CuO mixed powders since the value of ΔG_{MA} is larger than that of ΔG.
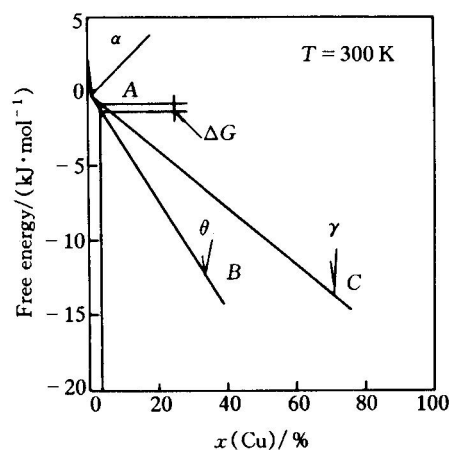
In addition, a kinetic constraint may

Fig.6 Schematic showing increase in free energy due to deviation from equilibrium

also prevent the formation of the equilibrium phase $CuAl_2$ in competition with the metastable phase Al_4Cu_9. Because ball-milling develops layer structure of elemental powders[13], the phases stability mechanism drew on layer diffusion pairs can be applied[16]. The stability of the intermetallic phases produced by heating two joined pure metals is related to the lattice mismatch δ between the intermetallic and the matrix phase. The local stress σ due to the lattice mismatch δ can be expressed as $\sigma = \mu\delta$, where, μ is the shear modulus and $\delta = 2|(a_1-a_2)/(a_1+a_2)|$ is the misfit, where a_1 and a_2 are the lattice parameters[17]. In the system studied, γ is of cubic $D8_3$ prototype structure, and δ_γ is calculated to be 0.73 ($a_\gamma = 0.870\ 52$ nm, $a_{Al} = 0.404\ 9$ nm, ignoring the change of the lattice constant of Al induced by the dissolution of Cu). θ is of BCC tetragonal C16 prototype structure with $a = 0.606\ 6$ nm, $c = 0.487\ 4$ nm. Assuming that the θ phase is precipitated from the Al matrix according to the habit plane, i.e. $(121)_\theta$ // $(111)_{Al}$, $[210]_\theta$ // $[110]_{Al}^{[18]}$, the value of δ_θ is calculated to be 1.30 on the habit plane, which is twice as much as δ_γ. Therefore, the strain energy induced by the precipitation of the γ phase is much smaller than that of the θ phase. This, together with the relative low value of ΔG (0.5 kJ/mol) for Al-10%CuO, provides a possible explanation for the formation of the metastable phase.

However, when the value of ΔG is too large for the kinetic constraint to function, the equilibrium phase will be obtained. Ball milling of Al-40% CuO (Al-14% Cu (mole fraction), $\Delta G = 2.5$ kJ/mol) has been carried out on the same conditions. The end products are composed of Al(Cu), Al_2O_3 and $CuAl_2$.

Other competing phases in the Al-Cu binary system includes η_1, η_2, ξ_1, ξ_2, ϵ_1, ϵ_2, β and χ. However, prototype structures or lattice parameters of these phases except η_1 and η_2 still remain unclear. The prototype structures of η_1 and η_2 (orthorhombic and end centered orthorhombic, respectively) are quite different from that of Al. So, it is reasonable that the γ-Al_4Cu_9 is the only existed metastable phase in the end products of Al-10% CuO alloy.

5 CONCLUSION

The reduction reaction of the Al-10% CuO mixed powders is induced by ball-milling. CuO is believed to be gradually reduced by Al, controlled by diffusion of atoms and ions. The reaction temperature is greatly lowered by ball-milling. Reduced Cu spontaneously reacts with Al to form a metastable equilibrium of Al(Cu) with Al_4Cu_9 phase during ball-milling, instead of $CuAl_2$ and Al(Cu), which is only observed after annealing.

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