

Formation of a TiB₂-Reinforced Copper-Based Composite by Mechanical Alloying and Hot Pressing

S.J. DONG, Y. ZHOU, Y.W. SHI, and B.H. CHANG

The microstructural changes during mechanical alloying and subsequent hot pressing of Cu, Ti, and B powder mixtures were studied using scanning electron microscopy, X-ray diffraction, differential thermal analysis, and electron microprobe analysis. In particular, the changes in the Cu grain size, lattice parameter, and lattice strain of the powder mixtures and the formation of new phases (TiCu₄ during mechanical alloying and TiB₂ during hot pressing) were investigated. The mechanism of the *in-situ* formation of TiB₂ particles in the resultant copper composite was also studied.

I. INTRODUCTION

A COPPER-BASED composite formed by dispersion strengthening with TiB₂ is a leading candidate for applications where an excellent combination of high thermal and electrical conductivity and high-temperature mechanical strength are required.^[1-5] Unlike the precipitation-strengthened copper alloys (such as Cu-Zr and Cu-Cr), Cu-TiB₂ maintains its strength up to very high temperatures because of the excellent thermal stability of the TiB₂ particles.^[2,4,6] The thermodynamic stability of the TiB₂ can also result in an extremely low residual content of Ti and B in the copper matrix, and, therefore, the composite exhibits a relatively high thermal and electrical conductivity.^[1,4]

Direct manufacture of Cu-TiB₂ from Cu and TiB₂ starting material does not yield composites with acceptable microstructural properties (*e.g.*, fine and uniformly distributed TiB₂ particles and strong interfacial bonding between the ceramic particles and the matrix).^[4,6] *In-situ* formation TiB₂ by reaction appears to be necessary, and several ways of doing this have been investigated.^[4,6] Chrysanthou and Erbaccio^[1] have studied *in-situ* formation of composites with up to 18 wt pct TiB₂ by carbothermic reduction of B₂O₃ in the presence of Cu-Ti melts and by mixing Cu-Ti and Cu-B melts. In the first method, the wetting between the ceramic particle and the matrix was poor due to the evolution of CO gas during the carbothermic reduction of B₂O₃. Only a partial reaction between the two melts was obtained in the second method, since a continuous TiB₂ layer prevented further mixing and, hence, further reaction between the two alloys. Poor ceramic particle distribution and coarse particle size are some of the major problems in those manufacturing processes, in which *in-situ* formation of ceramic particles occurs in liquid Cu alloys because of the density difference between TiB₂ and the Cu matrix.^[1,4] In this connection, Lee *et al.*^[4] have reported an improved spray-forming process, in which the ceramic particles are formed after deposition of droplets rather than formed in the Cu-Ti-B melt as in

conventional spray forming. This is very promising, since the size of the ceramic particles in Cu-TiB₂ formed by this improved process (termed reactive spray forming) was much finer than that in conventional spray-formed composites. However, the coarse particles were observed along dendrite cell boundaries, as compared with much finer and more uniformly distributed particles in the matrix.^[4]

Biselli *et al.*^[2] and Yuasa *et al.*^[5] have demonstrated the feasibility of fabricating composites with a fine, homogeneous distribution of TiB₂ particles by mechanical alloying followed by thermal treatment, although the mechanism of *in-situ* formation of TiB₂ was not very clear. For example, Yuasa *et al.*^[5] suggested that TiB₂ started to form in a powder mixture of Cu-4 wt pct Ti-2 wt pct B by solid-state reaction after 18.0 ks of milling. However, in another study of mechanical alloying of Cu-Ti-B powder mixtures to produce 5 to 20 vol pct of TiB₂, conducted by Biselli *et al.*,^[2] no evidence of TiB₂ formation was observed even after 180.0 ks of milling; the TiB₂ phase started to form only at a temperature near 873 K in a subsequent heat treatment. The purpose of this work is to study the formation of Cu-2 wt pct TiB₂ by mechanical alloying and subsequent hot pressing, with an aim to produce a Cu-TiB₂ composite with excellent electrical conductivity and high-temperature mechanical strength. The mechanism of *in-situ* formation of TiB₂ particles in the copper composite is also discussed.

II. EXPERIMENTAL PROCEDURE

Commercially available Cu (purity of 99.99 wt pct and particle size <150 μm), B (purity of 99.50 wt pct and particle size <44 μm), and Ti (purity of 99.70 wt pct and particle size <74 μm) powders were mixed to form Cu-1.38 wt pct Ti-0.62 wt pct B, with the aim of producing a Cu-2 wt pct TiB₂ composite. The Ti and B powders were equiaxed in shape, but the Cu powder particles were more platelike. Mechanical alloying was performed in a cylindrical ball mill rotating at 330 rpm and under an atmosphere of 99.99 wt pct argon. The container and the balls were made of austenitic stainless steel, and the container was water cooled. The balls were 10 mm in diameter, and the ball-to-powder weight ratio was 30:1. No process-control agent was used in ball milling). To monitor the effects of milling, a small quantity of milled powder was removed at intervals of 10.8 ks for further characterization. All powders were handled under an argon atmosphere to avoid oxidation.

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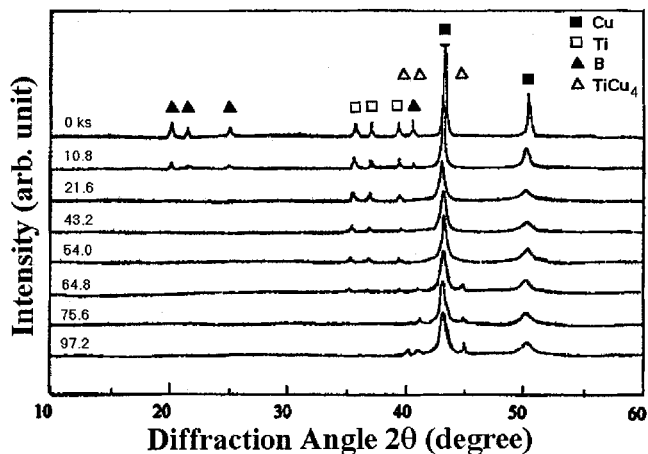


Fig. 1—XRD spectra of the Cu-Ti-B powder mixture after different ball milling times.

The ball-milled powders were analyzed by X-ray diffraction (XRD) with a D/max-3B diffractometer using Cu K_{α} radiation ($\lambda = 0.15418$ nm). The milled powder samples were also characterized using scanning electron microscope (SEM), a CRY-1-type differential thermal analysis (DTA) apparatus, and a JEM-100CX transmission electron microscope (TEM). The DTA measurements were performed under flowing argon at a heating rate of 5 K/min. For each DTA run, 30 to 40 mg of powders were hermetically sealed in a ceramic pan to allow a temperature excursion to 1223 K.

After mechanical alloying, the ball-milled powders were hot pressed in a graphite die in vacuum at 1073 to 1153 K for 9.0 ks under pressure of 50 MPa. The resultant samples were analyzed using a JXA-8800R electron microprobe analyzer.

III. RESULTS

A. Mechanical Alloying

The SEM was used to follow the evolution of particle morphology of the Cu-Ti-B powder mixture during mechanical alloying. The mean particle size of the powder mixture first increased to nearly 200 μm after 10.8 ks of milling and, subsequently, was continuously refined, reaching about 10 μm after 97.2 ks of milling. Multilayered structures were also observed in the powder mixtures during mechanical alloying; the internal layering was continuously refined with increased milling time until no layered structure was observed after 97.2 ks of milling. Overall, the changes in particle morphology observed in this work by the SEM and TEM are very similar to the general trends observed in other alloy systems during mechanical alloying.^[5,7,8]

Figure 1 shows the XRD spectra of the Cu-Ti-B powder mixture before milling (as blended) and after 10.8, 21.6, 43.2, 54, 64.8, 75.6 and 97.2 ks of milling. The intensities of the B and Ti diffraction peaks decreased with increased milling time, which is believed to be due to the dissolution of B and Ti into Cu. While the B peaks disappeared rapidly in the first few hours of milling, the dissolution of Ti was

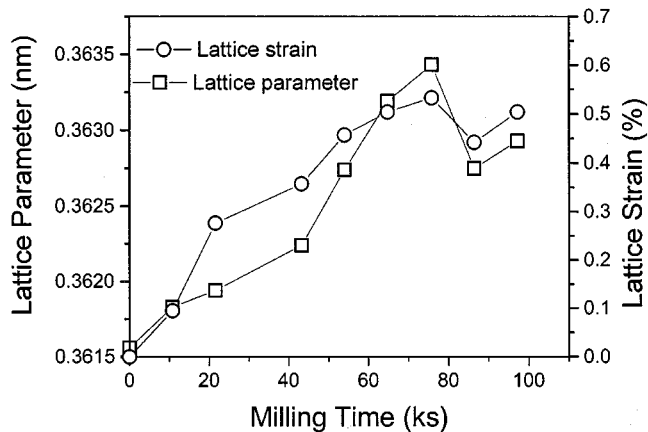
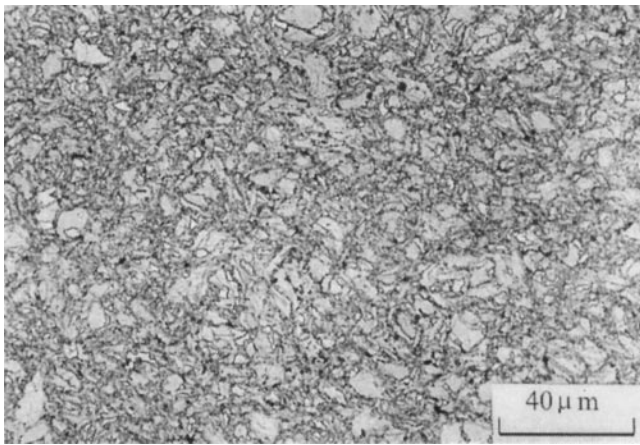


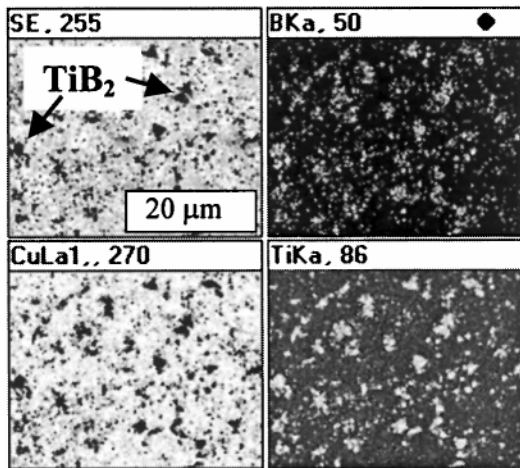
Fig. 2—The Cu lattice parameter and lattice strain of the Cu-Ti-B powder mixture vs ball milling time.

much slower: the Ti peaks were still obvious after 64.8 ks of milling. In a previous work by Yuasa *et al.*,^[5] the dissolution of Ti has also been observed during mechanical alloying of Cu-Ti-B powder mixtures, but it occurred at a much faster rate. With increased mechanical alloying time, the Cu diffraction peaks became broader and lower in intensity (Figure 1), and the peak locations also shifted to lower angles. These changes are indicative of a reduced grain size, increased stored strain energy, and increased average interatomic spacing due to dissolution of B and Ti, which has been also observed in other alloy systems.^[8,9] After 64.8 ks of milling, new diffraction peaks appeared (Figure 1), determined to be a result of the *in-situ* formation of the TiCu_4 phase. The exact composition of this phase has previously been debated:^[10] it was designated as TiCu_3 by Karlsson in 1951^[11] and, more recently, was confirmed as TiCu_4 .^[12] Figure 1 also shows that after 64.8 ks of milling, Ti peaks were still present while TiCu_4 was forming, but by 75.6 ks, only Cu and TiCu_4 peaks could be seen. At least on a macro scale, the solute dissolution process was sequential, with Ti starting to dissolve only after all the B was already dissolved (after 10.8 ks, Figure 1).

The grain size and internal strain were estimated from the broadening of the Cu (111) peak, and the lattice parameter was calculated from the shift in the Cu peaks.^[13,14] It was observed that the grain size continued to decrease with increasing milling time, from 52 to 27 nm after 97.2 ks of milling. The changes in the Cu lattice parameter and internal strain of the ball-milled powders are shown in Figure 2 as a function of the milling time. Both the lattice parameter and internal strain first increased with additional milling time, reaching maximum values at about 0.3635 nm for the lattice parameter and 0.53 pct for the lattice strain after 75.6 ks of milling, and then decreased during further milling. It is interesting to note the correlation between the changes in lattice parameter and internal strain. The lattice parameter of pure Cu is about 0.3613 nm. The maximum lattice strain in this work was much higher than that of milled pure Cu powders (0.2 pct), but was comparable to Cu-Fe powders.^[9,15] The decrease of the lattice parameter and lattice strain after 75.6 ks of milling is believed to be due to the precipitation of TiCu_4 (Figure 1). A similar behavior has been reported by Nagarjuna and Sarma.^[16]



(a)



(b)

Fig. 3—(a) Optical micrograph and (b) SEM micrograph and the corresponding B, Ti, and Cu dot-mapping images by EMPA of the Cu-TiB₂ composite milled for 97.2 ks and hot pressed at 1163 K for 9.0 ks.

B. Hot Pressing

The optimum hot-pressing parameters (1163 K for 9.0 ks under a pressure of 50 MPa) were determined from a series of hot-pressing experiments based on evaluating the density, electrical conductivity, and hardness of the resultant composites; the details will be documented elsewhere. The composite formed at the optimum conditions showed a microstructure with uniformly distributed dispersoids, which were rich in Ti and B (Figure 3) and were confirmed to be TiB₂ by XRD (Figure 4). The milling time and hot-pressing temperature required to form TiB₂ can be seen from the DTA curves of as-milled Cu-Ti-B powders (Figure 5). One exothermic peak in the range of 473 to 823 K was seen after 86.4 ks of milling, which is believed to be due to the recovery and recrystallization and/or further precipitation of TiCu₄; detailed work is needed to clarify this phenomenon. This low-temperature peak moved to lower temperatures with increasing milling time. After 97.2 ks of milling, another exothermic peak appeared in the range of 1098 to 1153 K, which is believed to correspond to the formation of TiB₂ (Figure 5), since TiB₂ was only observed in XRD of samples hot pressed at 1163 K, but not at 1073 K.

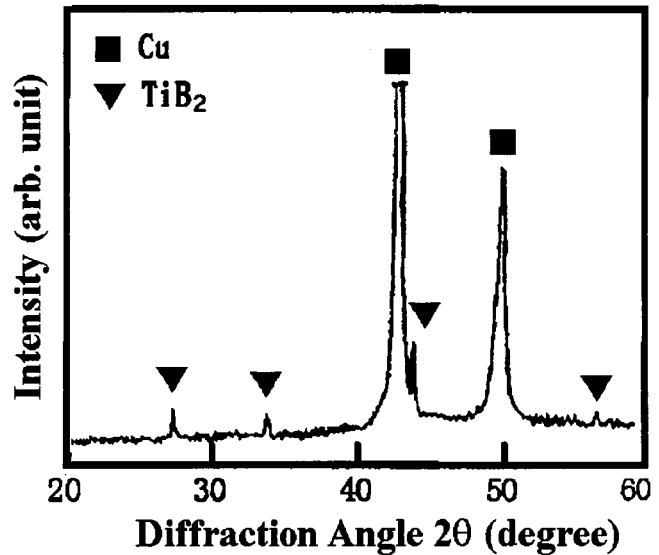


Fig. 4—XRD spectra of the Cu-TiB₂ composite milled for 97.2 ks and hot pressed at 1163 K both for 9.0 ks.

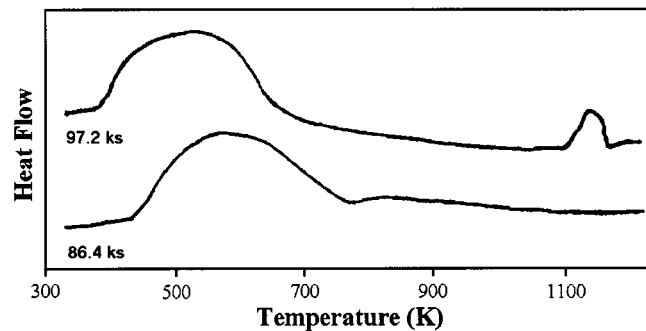


Fig. 5—DTA scans of the Cu-Ti-B powder mixture milled for 86.4 and 97.2 ks.

IV. DISCUSSION

A. Microstructural Changes during Ball Milling

Powder particles are subjected to high-energy collision during ball milling, which causes plastic deformation, cold welding, and fracture of the particles.^[8] Plastic deformation and cold welding are predominant during initial ball milling, in which the deformation leads to a change in particle shape, and cold welding leads to an increase in particle size and the formation of layered structures. As the ball milling is prolonged, the ability of the particles to accept further plastic deformation is diminished; therefore, fracturing becomes a significant process, which leads to a decrease in particle size until an equilibrium is reached between cold welding and fracturing. Repeated cold welding and fracturing continuously refined the layered structures until no layering was visible after 97.2 ks of milling.

Ball milling also reduces the Cu grain size to a nanometer scale. The mechanism for producing nanocrystalline powders by ball milling is governed by the severe plastic deformation introduced during ball milling.^[8] It has been suggested, for pure metals, that the ultimate grain size achievable by ball milling is determined by the minimum

grain size that can sustain a dislocation pileup within a grain and by the rate of recovery during ball milling.^[15] The addition of a second element to a pure metal increases the strength and hardness of the material,^[17] resulting in a smaller final grain size after milling.^[9] However, the grain size of the Cu-Ti-B powder mixture was at 27 nm after 97.2 ks of milling, which is larger than the minimum grain size of milled pure Cu powders reported at about 20 nm.^[15] While the exact reasons need to be further investigated, one possible explanation may be that the milling process in this work has not yet reached a steady state in terms of grain size.

Prolonged ball milling also increases the lattice parameter of Cu (Figure 2), which is closely related to the dissolution of B and Ti into Cu. This behavior was also observed in Fe-Cu systems.^[15]

The reduction in the Cu lattice parameter after 64.8 ks of milling should only occur if the solute (Ti) comes out of solution, which, in fact, is what occurs when TiCu₄ is precipitated (Figure 1). In this connection, Nagarjuna and Sarma^[16] have reported, in a study of the variation of the Cu lattice parameter in Cu-Ti alloys, that a drop in the lattice parameter was caused by the precipitation of Cu-Ti compounds.

In general, internal strain is caused by the difference in atomic size, accumulation of high dislocation density, and increased grain-boundary fraction.^[9,15] Eckert *et al.*^[15] argued, in a study on mechanical alloying of Cu-Fe powders, that the strain is caused mainly by the dislocation density introduced during milling. However, in the present work, the difference in atomic size is -24.2 pct between B and Cu and 14.8 pct between Ti and Cu (the atomic radii of B, Ti, and Cu are 0.097, 0.147, and 0.128 nm, respectively), which compares with the 1.5 pct difference between Fe and Cu in Eckert *et al.*'s work. Therefore, the contribution to the lattice strain from the size mismatch can be very significant, which, in fact, could be confirmed from the correlation between the lattice strain and lattice parameter in Figure 2, in which the precipitation of TiCu₄ has reduced both the lattice parameter and lattice strain.

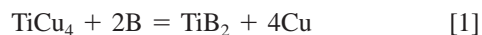
Boron has a solubility of 0.01 wt pct in Cu at room temperature and a maximum solubility of about 0.05 wt pct at 1286 K; Ti has a solubility of about 0.55 wt pct in Cu at room temperature and a maximum solubility of 6.5 wt pct at 1158 K.^[18] Therefore, mechanical alloying has enhanced the solubilities of Ti and B in Cu at low temperatures. Enhanced solubility has been also observed in many other systems (*e.g.*, in Fe-Cu^[9] and Co-B^[19]) during mechanical alloying and has been explained on the basis of the increased dislocation density and grain-boundary fraction.^[9] It is also interesting to note that Ti only started to dissolve into Cu after B was completely dissolved, at least on a macro scale. One of the possible reasons is that hard and brittle boron powder is highly fragmented from the very beginning of the milling process and is rapidly reduced to a fine dust, creating a fine dispersion of boron particles which are first able to interdiffuse through grain boundaries and then to enter the copper lattice.^[19] Another reason may be that B is easy to dissolve into Cu because B diffuses much faster as an interstitial element than Ti diffuses as a substitutional element. The dissolution of B into Cu increased the Cu lattice parameter, which could also make it easier for Ti to subsequently dissolve.

The delay in the start of TiCu₄ precipitation to after 64.8

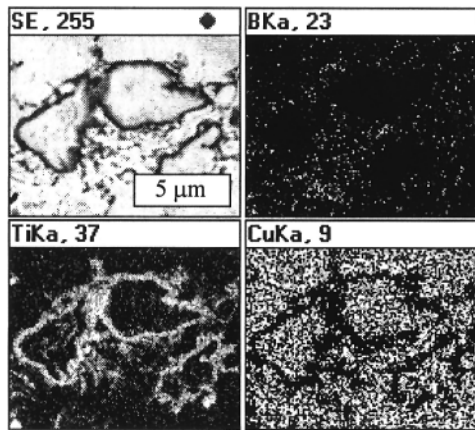
ks of milling (Figure 1) may be explained by the activation energy and concentration conditions required for forming TiCu₄. It has been pointed out that the mechanically stored enthalpy of increased internal strain and grain-boundary fraction (due to refined grain size) during ball milling can serve as a driving force for forming a new phase.^[9] An increase in the grain-boundary fraction and internal defects should also enhance diffusion by providing fast diffusion paths at low temperatures, which is required for the reaction to occur. Increasing the milling time can increase this mechanical activation, which may be why there is a minimum ball-milling time required for TiCu₄ to form and why the precipitation increased as the ball-milling time increased. The fact that no TiCu₄ formed until 64.8 ks of ball milling would be also related to the buildup of Ti concentration required for forming the TiCu₄ phase. The Ti concentration in Cu required to form TiCu₄ may have been only reached after 64.8 ks of milling. It was thought that formation of TiCu₄, but not TiB₂, during mechanical alloying may be explained by the lower activation energy required to be overcome to form TiCu₄ compared with that required to form TiB₂. Unfortunately, no data for the activation energy for TiCu₄ were found, while the activation energy of 733 kJ/mol for sintering of TiB₂ has been reported.^[20]

B. *In-Situ* Formation of TiB₂

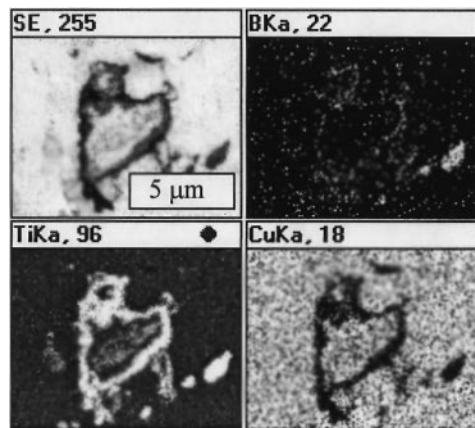
TiB₂ was not formed during milling; however, TiCu₄ was replaced by TiB₂ during subsequent hot pressing at 1163 K for 9.0 ks (Figure 4). This is because TiB₂ is thermodynamically more stable than TiCu₄.^[21] The electron microprobe analysis area mapping of a sample after milling for 86.4 ks and hot pressing at 1073 K for 9.0 ks has clearly shown that the B segregation is near but not exactly aligned with areas of high Ti concentration (Figure 6(a)). This indicates that after these processing steps, Ti still existed in a form of Ti/Cu alloy rather than in a form of Ti/B compound, which is consistent with the previous observations by XRD (Figure 4) and DTA. After milling for 97.2 ks and hot pressing at 1163 K for 9.0 ks (Figure 6(b)), the B segregation is seen to be exactly aligned with the Ti high-concentration areas, which indicates that TiCu₄ has converted into a Ti/B compound: TiB₂, as confirmed by XRD (Figure 4). Therefore, the *in-situ* formation of TiB₂ may be described by the following reaction:



The activation energy required to be overcome to form TiB₂ could come from mechanical energy acquired during milling and/or thermal energy acquired during subsequent heat treatment. The fact that TiB₂ forms at 1098 to 1153 K during heating after 97.2 ks of milling but not after 86.4 ks of milling (Figure 5) indicates that there is a minimum requirement for the mechanical energy acquired during ball milling to promote the formation of TiB₂ during subsequent heating to 1223 K. Above the minimum value, the increased mechanical energy acquired should lead to a lower thermal-energy requirement to complete the reaction, which means that the high-temperature exothermic peaks (corresponding to the TiB₂ precipitation) in Figure 5 could shift to lower temperatures as the milling time increases, or *vice versa*. A similar behavior has been observed by Corrias *et al.*^[19] during thermal treatment of ball-milled Co-B powders, in which



(a)



(b)

Fig. 6—SEM micrograph and the corresponding B, Ti, and Cu dot-mapping images of the Cu-TiB₂ composite milled for 97.2 ks and hot pressed at (a) 1073 K and (b) 1163 K both for 9.0 ks.

the formation of t-Co₂B shifted to lower temperatures as the milling time increased.

The effect of mechanical alloying on the formation of TiB₂ can be best described using a schematic diagram of the potential energy for the formation of TiB₂ (Figure 7). The term E_0 is the initial energy level of the Cu-Ti-B mixture. The activation energy required to be overcome to form TiB₂ is the sum of E_{MA} and E_{Th} , which are the mechanical energy acquired during milling and the thermal energy acquired during subsequent heating, respectively. A higher E_{MA} value would lead to a lower E_{Th} value, or *vice versa*. The precipitation of TiCu₄ during mechanical alloying also results in nearby B segregation, which may create the concentration conditions for forming TiB₂ during hot pressing (Figure 6(a)).

Yuasa *et al.*^[5] claim to have observed the formation of TiB₂ during ball milling in a study of mechanical alloying of a Cu-4 wt pct Ti-2 wt pct B powder mixture. On the other hand, Biselli *et al.* have reported, in a study on Cu-5 vol pct (Ti + 2B) mixtures, that TiB₂ was only observed after annealing at 873 K following ball milling, but not during mechanical alloying even after 180 ks of milling.^[2] The reason for these differences in the energetics of formation of TiB₂ may be due to the different mechanical-alloying and heat-treatment conditions and the different Ti and B

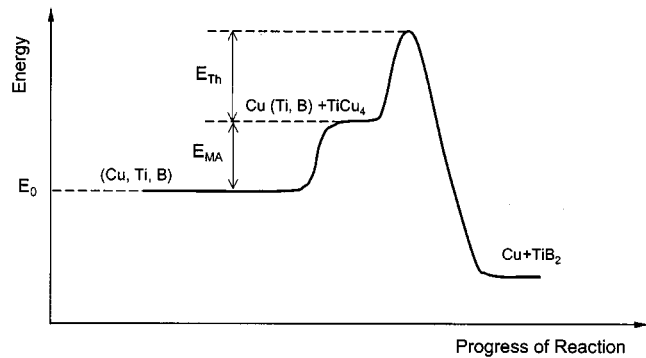


Fig. 7—Schematic of potential energy diagram for the formation of TiB₂.

concentrations between the present work and that of others.^[2,5] For example, the rotation speed of the mill and the ball-to-powder weight ratio were 500 rpm and 100:1 in Yuasa *et al.*'s work,^[5] as compared to the values of 330 rpm and 30:1 in this work. When the milling intensity is increased either by increasing the ball-to-powder weight ratio and/or by increasing the speed of collision, more energy will be transferred to the powder particles and, hence, may be available for new phase formation.^[8] As shown in Figure 7, as the energy obtained during ball milling increases, the thermal energy required to exceed the activation energy requirement for formation of TiB₂ during subsequent heating should be reduced. The *in-situ* formation of TiB₂ during ball milling could even occur if the energy absorbed by the powder is larger than the activation energy required to form TiB₂. This may explain why TiB₂ was observed during ball milling in Yuasa *et al.*'s work.^[5] When the mechanical energy acquired during ball milling is not sufficient to overcome the activation energy to form TiB₂, additional thermal-activation energy must be provided by subsequent heating. For the same reason, an increase in the mechanical energy acquired should reduce the required thermal activation (*i.e.*, reduce the minimum heating temperature), which may be the reason for the difference in temperatures at which TiB₂ is formed as identified in this work and in Biselli *et al.*'s work.^[2]

V. SUMMARY

In this work, the formation of a Cu-2 wt pct TiB₂ composite by mechanical alloying and subsequent hot pressing has been investigated by SEM, XRD, DTA, and electron microprobe analysis. The results have shown that the powder mixture of Cu, Ti, and B underwent severe plastic deformation, cold welding, and fracture due to the collision of milling balls during mechanical alloying. Prolonged ball milling resulted in extremely fine Cu grains with a large internal strain. The solubility of B and Ti in Cu was greatly enhanced during mechanical alloying, which resulted in an increased Cu lattice parameter. The precipitation of TiCu₄ during ball milling decreased the Cu lattice expansion and, hence, the internal strain, which was caused by the dissolution of B and Ti into Cu. Differential thermal analysis has shown that the *in-situ* formation of TiB₂ occurred in the temperature range of 1098 to 1153 K after 97.2 ks of milling, which is believed to result from the reaction between TiCu₄ and B. The mechanism of the *in-situ* formation of TiB₂ particles in the copper composite was also discussed.

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