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In-situ Synthesis of Cu-TiB_2 Nanocomposite by MA/SPS

Young-Soon Kwon, Ji-Soon Kim, Hwan-Tae Kim, Jin-Soo Moon, D.V. Dudina* and O.I. Lomovsky*
Research Center for Machine Parts and Materials Processing, University of Ulsan 680-749, Korea
**Institute of Solid State Chemistry and Mechanochemistry, SB RAS, Novosibirsk*
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Abstract Nano-sized TiB_2 was in situ synthesized in copper matrix through self-propagating high temperature synthesis (SHS) with high-energy ball milled Ti-B-Cu elemental mixtures as powder precursors. The size of TiB_2 particles in the product of SHS reaction decreases with time of preliminary mechanical treatment ranging from 1 in untreated mixture to 0.1 in mixtures milled for 3 min. Subsequent mechanical treatment of the product of SHS reaction allowed the TiB_2 particles to be reduced down to 30−50 nm. Microstructural change of TiB_2-Cu nanocomposite during spark plasma sintering (SPS) was also investigated. Under simultaneous action of pressure, temperature and electric current, titanium diboride nanoparticles distributed in copper matrix move, agglomerate and form a interpenetrating phase composite with a fine-grained skeleton.

Keywords : Titanium diboride, Copper matrix, Nanoparticles, Spark-Plasma sintering, Mechanical alloying

1. Introduction

Titanium diboride is a unique reinforcement for copper and its alloys because of its high melting point, high hardness and excellent thermal and electrical conductivities.

Most of the recent studies on the properties and fabrication methods of TiB_2 reinforced copper are directed to the in situ composites[1-5]. Lee *et al.*[1] reported on the formation of TiB_2-Cu MMC by spray forming. In the work of Tu *et al.*[2] copper was reinforced by TiB_2 formed via reaction of B_2O_3 with carbon and titanium in Cu-Ti melt. These methods yield Cu-TiB_2 composite with uniformly distributed titanium diboride in copper matrix. However, these methods require complex equipment and are expensive for industrial scales. Considerable efforts have been made to synthesize Cu-TiB_2 composite via mechanical alloying. Different opinions are presented in literature on the feasibility of direct formation of TiB_2 phase in copper matrix during mechanical treatment[3-5]. Yuasa *et al.*[3] have shown that TiB_2 starts to form by solid-state reaction in powder mixture of Cu, Ti and B after 5 hours of milling. However, Biselli *et al.*[4] have demonstrated the absence of TiB_2 phase in Cu-Ti-B mixture after 50 hours of mechanical alloying. Similar results have been reported by Dong *et al.*[5] showing no evidence of TiB_2 formation in copper matrix after 25 hours of mechanical treatment.

It is known that formation of titanium diboride from elements is accompanied by evolution of large amount of heat (ΔH^0_{298}=293 kJ/mol)[6]. Due to this effect TiB_2 can be successfully produced from elements via self-propagating high-temperature synthesis (SHS). SHS is extremely attractive with short time of synthesis, low energy consumption and high purity of products as its main advantages.

Interpenetrating phase composites(IPCs) are considered as a new class of materials different from traditional composites. In IPCs the constituent phases are tri-dimensional continuous networks interpenetrating each other[7]. IPCs offer a high potential for creating materials with beneficial combination of properties and multifunctional characteristics.

The most common method used to produce these structures in "metal matrix-ceramic reinforcement" systems is infiltration of pre-existing reinforcing porous preforms with molten metal[8]. The preforms are required to be of uniform spatial distribution of pores with desired size. It is understood that structure with extremely small pores (submicron and nanopores) is difficult to produce.

In the present study, in situ formation of TiB_2 particles in Cu matrix through combination of mechanical

treatment and SHS were investigated. And also studied the microstructure of SPSed Cu-TiB_2 powder compact to find out the effectiveness of these procedure for production of IPCs.

2. Experimental Details

Titanium (99,5% purity, 10 μm, irregular), amorphous boron (97% purity, <1 μm) and copper powders (99,7% purity, 40 μm, dendrite) were used as raw materials. Compositions (Ti-2B)+n%wt. Cu, where n varied from 0 to 70, were studied. Powder mixtures were treated in high-energy ball mill AGO-2 (planetary mill type) with ball acceleration 600 $m \cdot s^{-2}$. Balls and vials made of stainless steel were used. The diameter of balls was 5 mm. The powder/balls ratio was 1/20 and remained constant in all experiments. The vials were pumped and filled with argon up to 0.3 MPa.

Powder precursors obtained via mechanical treatment of initial mixtures were subjected to SHS reaction which was ignited by means of nickel-chromium spiral heated by electric current. SHS-reaction was carried out in argon atmosphere.

Combustion rate and combustion temperature were measured by tungsten-rhenium thermocouple of 100 μm diameter.

Phase content of mechanically treated mixtures and SHS-products were studied with X-ray phase analyzer DRON-3. Co Kα radiation was used.

Morphology of the products was studied by scanning electron microscopy (SEM) using JSM-T20 and JSM-6500F (Field Emission SEM) "JEOL" microscopes.

Nano composite powder compacts were spark plasma sintered in a vacuum atmosphere. Graphite mold of 10 mm diameter was used. The applied SPS-pressure was 50–70 MPa. SPS-temperature varied in the range 700–950°C. It should be noted that effective temperature of the sample is usually 50°C higher than SPS-temperature measured by thermocouple inserted in the wall of the mold. Holding time at the maximum temperature was 0–30 min.

3. Results and Discussion

Morphology changes during mechanical treatment of Ti-B-Cu mixtures were studied by scanning electron microscopy. After 2 min of mechanical treatment, the major part of the sample consists of

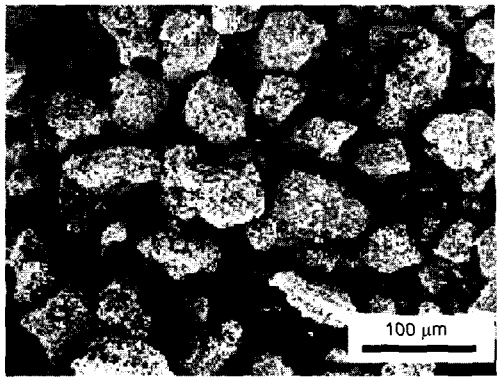


Fig. 1. Agglomerates formed after 2 min of mechanical treatment in (Ti-2B)-60% wt. Cu mixture.

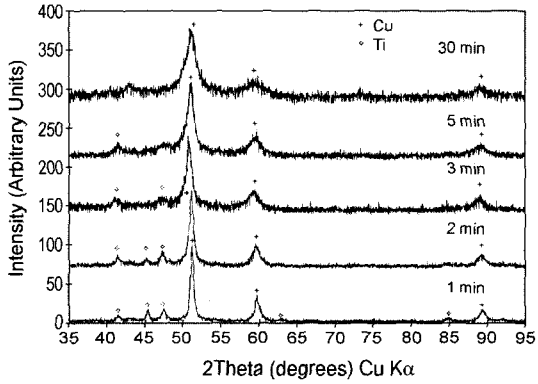


Fig. 2. XRD patterns of (Ti-2B)-60% wt. Cu samples mechanically treated for 1, 2, 3, 5 and 30 min.

agglomerates of 50–100 μm (Fig. 1). As the time of treatment increases, the size of the agglomerates increase to reach several hundreds micron. The surface of the agglomerates becomes denser but the inner part is still characterized by spongy structure showing that large agglomerates consist of relatively small ones. Thus, it is evident that during mechanical treatment composite particles with several levels of heterogeneity are formed, interfaces between the reagents being significantly increased.

XRD patterns of (Ti-2B)-60%wt. Cu composition milled for 1, 2, 3, 5 and 30 min are shown in Fig. 2. It is seen that TiB_2 is not formed during mechanical treatment. Analyzing the changes in XRD patterns one can conclude that mechanical treatment is associated with copper grain refinement, lattice strain accumulation and possibly dissolution of titanium in copper.

Fig. 3 shows that combustion rate vs. time of preliminary mechanical treatment is described by curve

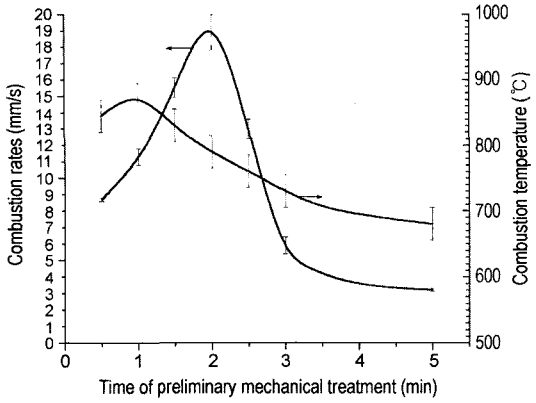


Fig. 3. Combustion temperature and combustion rate for (Ti-2B)-60%wt. Cu vs. time of preliminary mechanical treatment.

with peak value. The increase of combustion rate can be explained by the significant dispersion of the reagents, increased interfaces and high defects concentrations.

The decrease of combustion rate is likely to be due to formation of supersaturated solid solutions of titanium in copper[9], as well as recovery processes that may occur during prolonged mechanical treatment. It was demonstrated[10] that the temperature rise during treatment could cause recovery processes, moreover, in some cases grain growth occurs.

Fig. 3 also indicates that combustion temperature in mechanically treated mixtures is lower than copper melting point. Experiments with untreated mixtures have shown that combustion in untreated mixtures proceeds at temperatures higher than copper melting point and limited by its boiling point. It was observed that the walls of SHS-reactor were covered with condensed copper. Thus, one can conclude that preliminary mechanical treatment significantly reduces combustion temperatures and brings copper losses by evaporation to minimum levels.

In order to study the possible reasons for the decrease of combustion temperature DTA and DSC analyses were performed. Untreated mixtures showed the only exothermic peak at 880°C associated with thermal explosion. As is seen from Fig.4 heat release in mechanically treated mixtures begins at lower temperatures (100°C) and proceeds in several stages. So, the rate of heat release is decreased and combustion temperature is reduced. Moreover, ignition temperature is also decreased. In the Ref. [11] it is shown that

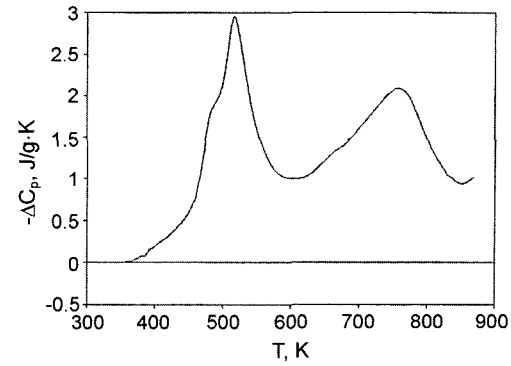


Fig. 4. DSC curve for (Ti-2B)-60%wt. Cu, mechanically treated for 2 min.

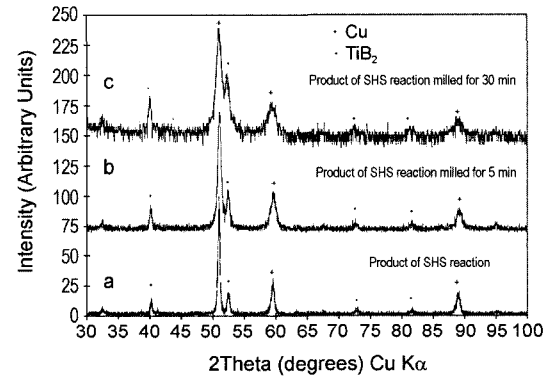


Fig. 5. XRD patters of the products of TiB_2-60%wt. Cu composition as-obtained after SHS-reaction (a) and after subsequent mechanical treatment for 5 min (b) and 30 min (c).

the first exothermic effects in mechanically treated samples are due to recovery processes.

XRD pattern of the product of SHS-reaction of TiB_2-60%wt. Cu composition is shown in Fig. 5a. It is evident that the product consists of titanium diboride and copper.

The products of SHS-reaction were studied by scanning electron microscopy. As an example Fig. 6 demonstrates the product of SHS-reaction of TiB_2-60%wt. Cu composition. Microstructural feature of the composite is a uniform distribution of submicron TiB_2 particles (0.1−0.5 μm) in copper matrix. Formation of submicron particles is the consequence of mechanical treatment because the products of SHS-reaction in untreated mixtures contain particles more than 1 μm in size[12].

Submicron size is not the limit for particles formed

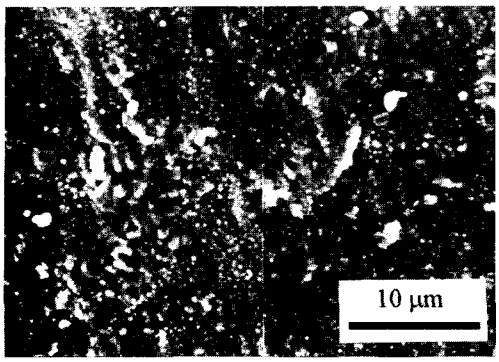


Fig. 6. SEM image of the product of SHS reaction of TiB_2-60% mass.Cu composition (time of preliminary mechanical treatment is 2 min).

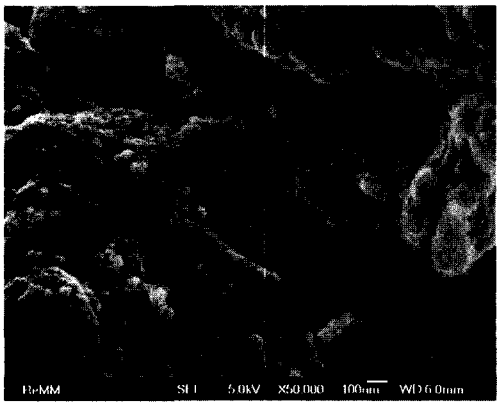


Fig. 7. Field Emission SEM image of the sample of TiB_2-60% mass.Cu composition milled for 30 min after SHS reaction.

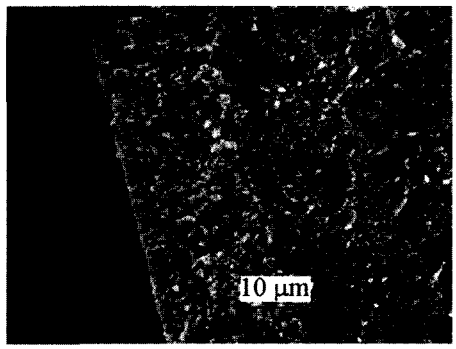
in situ in metal matrix. Mechanical treatment of the product of SHS reaction causes the size of TiB_2 particles to decrease. Fig. 5b,c shows XRD-patterns of the products of SHS reaction of (Ti-2B)-60%wt.Cu composition milled for 5 and 30 min. From XRD peak broadening the size of TiB_2 and Cu grains are estimated to reach 30 nm. Field Emission SEM image of the product milled for 30 min is shown in Fig. 7. It is seen that the average size of particles in the composite is about 50 nm that is in agreement with XRD estimation. It is believed that in certain milling conditions even smaller particles can be obtained.

Spark Plasma Sintering[13] involves simultaneous action of pressure, temperature and pulse electric current. These conditions allow for efficient sintering in short time with retention of fine microstructure of starting powders to a marked extent.

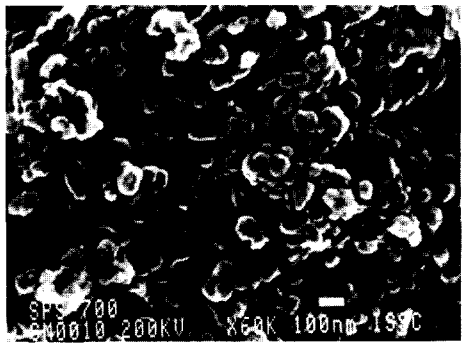
It is not correct to compare temperature conditions in conventional sintering and Spark-Plasma Sintering because in the former case the temperature is more or less uniform within the sample under heating while in SPS local high-temperature regions are generated due to spark formation between particles. Moreover, quick cooling of intergranular bonding due to pulse current regime introduces high degree of non-equilibrium in the sintering process. So, these two methods of sintering should be considered separately.

Polished and etched surface of SPS-compacts showed fine two-phase microstructure. The samples sintered at 950°C contained regions corresponding to melted copper, however, as was proved by EDS analysis, the major part of all SPS-compacts was represented by copper and titanium diboride tightly interconnected with each other.

The connectivity between TiB_2 particles was observed when we removed copper matrix from the surface of SPS-compacts by electrochemical etching and formed a layer (Fig. 8a). X-ray phase analysis



(a)



(b)

Fig. 8. (a) Electrochemically etched surface, (b) Titanium diboride skeleton of SPS-compact.

showed that this layer consisted of titanium diboride. It is seen that the layer has a porous fine-grained network structure. Detection of this layer is the evidence of connectivity between titanium diboride particles.

It is worth noting that TiB_2 layer is revealed under electrochemical etching on all SPS-compacts of this composition sintered at different temperatures despite substantial difference in their porosity. The part of melted copper in the compacts increased with the temperature, therefore, there can be an argument on the role of molten copper in the formation of the skeleton. However, the sample sintered at 700°C shows no evidence of copper melting but exhibits titanium diboride skeleton. Consequently, connectivity of titanium diboride particles should be considered as specific feature of SPS-processing.

As is seen from Fig. 8b titanium diboride skeleton remains fine-grained with the size of crystallites less then 100 nm. Thus, it can be concluded that peculiarities of SPS compaction is retention of nanostructure in bulk state and formation of titanium diboride skeleton.

In the Ref. [7] it was proposed to consider such structures as interpenetrating phase composites (IPCs). The most common method being used now to produce these structures in metal matrix-ceramic reinforcement systems is infiltration of pre-existing reinforcing porous preforms with molten metal[8]. The preforms are required to be of uniform spatial distribution of pores with desired size. Starting from nanocomposite powders containing high content of nanoparticles and using SPS-consolidation it becomes possible to obtain nanostructured IPC.

4. Conclusions

1. Preliminary mechanical treatment of titanium, boron and copper powder mixtures allows copper content in mixtures capable of SHS reaction to be increased up to 70% wt.

2. Combustion and ignition temperatures in mechanically treated precursors are lower compared to untreated mixtures.

3. The average size of TiB_2 particles formed in copper matrix during SHS reaction ranges from 0.1 to 0.5 μm.

4. Mechanical treatment of the product of SHS reaction results in nanocomposite with TiB_2 particles of 30−50 nm.

5. Microstructure evolution during sintering of titanium diboride-copper nanocomposites with high volume content of TiB_2 nanoparticles (up to 57%), microstructural changes proceed through different paths depending upon the process by which sintering is stimulated. Simultaneous action of electrical discharges, pressure and temperature on the composite during Spark-Plasma Sintering results in high degree of densification and formation of titanium diboride skeleton interpenetrating copper matrix.

Acknowledgements

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