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TiB_2-Cu Interpenetrating Phase Composites Produced by Spark-plasma Sintering

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Abstract Interpenetrating phase composites of TiB_2-Cu system were produced via Spark-Plasma Sintering (SPS) of nanocomposite powders. Under simultaneous action of pressure, temperature and electric current titanium diboride nanoparticles distributed in copper matrix move, agglomerate and form a fine-grained skeleton. Increasing SPS-temperature and holding time promote densification due to local melting of copper matrix. When copper melting is avoided the compacts contain 17–20% porosity but titanium diboride skeleton is still formed representing the feature of SPS. High degree of densification and formation of titanium diboride network result in increased hardness of high-temperature SPS-compacts.

Key words : Titanium diboride, Copper matrix, Interpenetrating phase composites, Spark-plasma sintering

1. Introduction

Interpenetrating phase composites (IPCs) are considered as a new class of materials different from traditional composites. The latter usually consist of a matrix and discrete reinforcement phases shaped as particles, whiskers or fibers. In IPCs the constituent phases are tri-dimensional continuous networks interpenetrating each other[1]. 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[2]. 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.

Required size of network grains can be achieved when IPC is obtained through consolidation of "matrix-reinforcement" composite powders with high volume content of ceramic phase. In this case fine ceramic dispersions could ensure formation of fine-grained skeleton when appropriate method of consolidation is found. The method should probably include simultaneous action of temperature and pressure to form continuous skeleton from separate particles making it possible at the same time to retain fine-grained microstructure.

These requirements can be satisfied by Spark Plasma Sintering (SPS)[3], which involves simultaneous action of pressure, temperature and pulse electric current. Pulse DC passing through the sample promotes formation of local high-temperature regions and ensures quick cooling of integranular bonding allowing uniform and efficient sintering in short time retaining fine microstructure of starting powders to a marked extent.

In the present study we sintered Cu-57 vol.% TiB_2 composite powders containing titanium diboride nanoparticles using Spark Plasma Sintering and investigated microstructure of bulk material to find out the effectiveness of this procedure for production of IPCs.

2. Experimental

To obtain Cu-57 vol.% TiB_2 nanocomposite powders methods of mechanical alloying and self-propagating high-temperature synthesis were combined[4]. Ti-B-Cu powder mixtures were mechanically treated in high-energy planetary ball mill AGO-2[5] with stainless steel balls of 5 mm diameter and steel vials. The powder/balls weight ratio was 1/20 in all experiments. Before milling the vials were evacuated and filled with argon to prevent oxidation during processing. SHS-reaction was carried out in mechanically alloyed Ti-B-Cu mixture and was also performed under argon atmosphere. The product of SHS reaction containing submicron TiB_2 particles distributed in copper matrix was subjected to subsequent mechanical treatment resulting in the decrease of TiB_2 particle size down to nano-level. After the procedure described above the composite powders with titanium diboride particles 30–50 nm in size distributed in copper matrix were obtained.

Nanocomposite powders were spark-plasma sintered. Graphite mold of 10 mm was used. Sintering was performed in vacuum. 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 was 0–30 min. To prepare the samples for microstructure observations sintered compacts were polished and etched with $FeCl_3$-H_2O-ethyl alcohol solution. Prepared samples were observed and analyzed by Field Emission Scanning Electron Microscopy (FE SEM, JEOL JSM 6500F) and Energy Dispersive Spectroscopy (EDS). To observe the titanium diboride 3D network an electrochemical etching of the surface layer was performed in HNO_3-methyl alcohol solution for removing copper matrix.

MVK-H1 Hardness testing Machine was used for Vickers hardness measurements.

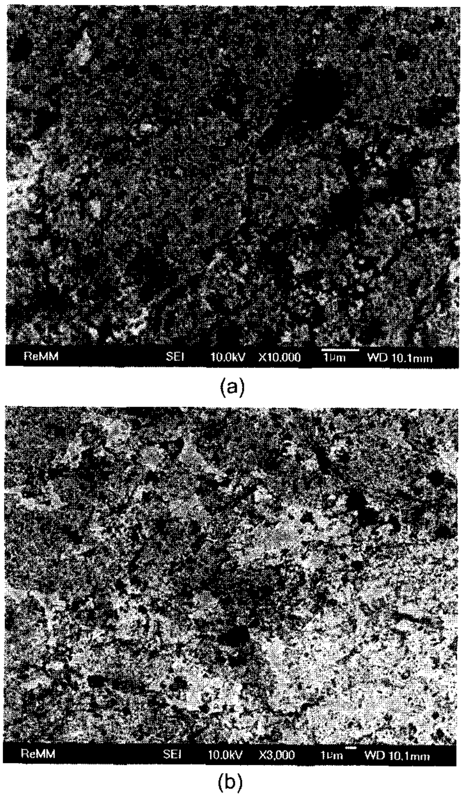
3. Results and Discussion

Fig. 1 illustrates TEM microstructure of TiB_2-Cu nanocomposite. It is seen that titanium diboride particles are distributed in copper matrix more or less uniformly with local regions containing accumulation of particles. This kind of distribution appears to favor agglomeration under pressing and sintering.

In SPS process sintering occurs through electrical discharges between particles, which result in formation of high-temperature regions so that melting can occur.

Field Emission SEM images of SPS-compacts are presented in Fig. 2. EDS analysis has shown that light regions in the sample sintered at 950°C (Fig. 2,a) correspond to copper phase with negligible content of titanium diboride. Dark particles 2–4 μm in size were confirmed to be TiB_2 agglomerates formed due to poor wettability of titanium diboride with molten copper. Such agglomerates were not observed when copper melt-

Fig. 1. TEM image of Cu-57 vol.% TiB_2.



(a)

(b)

Fig. 2. Field Emission SEM images of Spark Plasma Sintered compacts: a-700°C, 70 MPa, 5 min; b-950°C, 70 MPa, 30 min.

Table 1. Relative density and Vickers hardness of SPS-compacts

SPS-temperature (°C)*	Holding time (min)	SPS-pressure (MPa)	Relative density (%)	HV
700	5	70	79.4	237
800	5	70	83.0	332
950	0	50	88.8	584
950	5	50	90.0	–
950	0	70	87.7	–
950	5	70	89.9	–
950	30	70	93.9	673

ing was avoided at lower SPS-temperature (Fig. 2,b). However, substantial porosity remained in the sample sintered at 700°C (Table 1).

EDS analysis proved that the major part of all SPS-compacts was represented by copper and titanium diboride tightly interconnected with each other.

To study the connectivity between TiB_2 particles we removed copper matrix from the surface of SPS-compacts by electrochemical etching and formed a layer (Fig. 3). X-ray phase analysis showed that this layer consisted of titanium diboride as the major phase with small amounts of $TiBO_3$ probably formed as a result of electrochemical reaction. 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.

Hardness of SPS-compacts is defined by the presence of TiB_2 skeleton as well as by degree of densification (Table 1).

It is worth noting that formation of TiB_2 layer under electrochemical etching was showed up on all SPS-compacts obtained in this study. The samples substantially differed in porosity (Table 1) and the part of melted copper increasing with temperature. Consequently, connectivity of titanium diboride particles should not be attributed to densification but to specific features of processing during SPS-sintering.

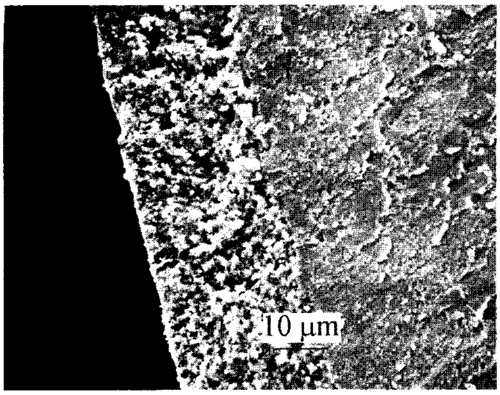


Fig. 3. Electrochemically etched surface of SPS-compact showing titanium diboride skeleton.

To prove this assumption we conventionally sintered pre-pressed Cu-57 vol.% TiB_2 tablets. Sintering was performed under argon atmosphere at 950°C. Agglomerates with different shapes and several microns in size were confirmed by scanning electron Microscope. Electrochemical etching of these tablets did not reveal any layer, the products of etching having weak adhesion to initial material. Thus, no spatial connectivity of TiB_2 particles can be obtained by conventional sintering.

Process of formation of titanium diboride skeleton seems to include moving of titanium diboride particles as a whole in solid copper matrix. Coalescence of particulate inclusions in high-strained metal matrices by their moving, collisions and agglomeration is described in[6)]. Such phenomenon can take place in non-uniform fields of stresses and temperatures. In the case of SPS simultaneous action of pressure, temperature and pulse electric current generating spark impact pressure and local stresses may force titanium diboride particles move within copper matrix which in its turn contains high concentrations of defects resulted from peculiarities of preparation of the powder nanocomposite. This mechanism does not exclude coalescence and grain growth through diffusion processes.

4. Conclusions

1. Spark Plasma Sintering of "metal matrix-ceramic reinforcement" nanocomposite powders with high volume content of ceramic particles enables producing bulk composite with interpenetrating phase microstructure. Under simultaneous action of electric current, temperature and pressure titanium diboride particles move within

high-strained copper matrix to form fine-grained agglomerated network.

2. Increasing SPS-temperature and holding time promote densification due to local melting of copper matrix. When copper melting is avoided the compacts contain 17–20% porosity but titanium diboride skeleton is still formed.

3. Formation of titanium diboride skeleton and high degree of densification result in high hardness of the compacts.

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