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Microstructure changes in TiB_2-Cu nanocomposite under sintering

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Stability and growth of nanoparticulate reinforcements in metal matrix composites during heating are widely studied for dispersion-strengthened alloys, which contain several volume percent of reinforcing phase. When high volume content of nanoparticles distributed within a matrix is concerned results of particles aggregation and growth as well as crystallization mechanisms are not so evident. In this work microstructural evolution under sintering in metal-matrix composite TiB_2-Cu with high volume content (up to 57%) of titanium diboride nanoparticles 30–50 nm in size was investigated. The nanocomposite powders were produced through synthetic method combining preliminary mechanical treatment of initial powder mixtures in high-energy ball mill, self-propagating exothermic reaction and subsequent mechanical treatment of the product. We focused on microstructure changes in TiB_2-Cu nanocomposite consolidated by Spark-Plasma Sintering and conventional sintering and showed that in the former case fine-grained skeleton of titanium diboride is formed with connectivity between particles well established. In the latter case behavior of nanoparticles is surprising: at low temperatures fiber-like structures are formed while increasing temperature causes appearance of faceted crystals. These unusual results allow us to propose the direct involvement of nanoparticles in the processes of crystallization by moving as a whole in the matrix.

1. Introduction

Increased interest to properties of nanomaterials requires stability and evolution of nanostructure under a variety of conditions to be studied. This covers evaluation of stability under increasing temperature, changes during consolidation from powder state and processes involved in the performance of nanomaterial.

In this paper we studied peculiarities of nanostructure evolution in TiB_2-Cu nanocomposite. This system was chosen for investigations due to unique combination of the properties of constituent phases. TiB_2 exhibits high melting point, high hardness and in contrast to other ceramics it is thermally and electrically conductive. TiB_2-Cu composites were obtained in a number of works [1–4] with the goal to produce dispersion-strengthened copper as potential material for electric contacts. Materials combining high-temperature stability and thermal conductivity can be also obtained on the basis of TiB_2-Cu system. In this case a side of a bar subjected to high temperatures is made of titanium diboride while the opposite one being cooled is made of copper, distribution of elements through the bar being continuous [5]. Therefore, not only dispersion-strengthened alloys of this type are of interest but functionally gradient materials as well.

Methods of mechanical treatment in high-energy ball mills have shown promise in preparation of powder nanomaterials [6]. When compounds are obtained, which are formed through highly exothermic reactions it is efficient to use mechanical treatment together with conventional self-propagating high-temperature synthesis (SHS). We obtained TiB_2-Cu nanocomposite combining self-propagating exothermic reaction with preliminary and subsequent mechanical treatment of the powders [7]. Conditions for SHS-reaction to proceed are satisfied by high exothermity of titanium diboride formation. SHS-reaction in this system gives no phases other than required (no Cu-Ti intermetallics or borides other than TiB_2). This kind of processing makes it possible to obtain very high concentrations (more than 50 vol%) of reinforcement particles of extremely small (nano) size.

So, two tasks can be allotted: to determine conditions of compaction allowing for nanostructure retention and

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to find what distinctive structures can be obtained when nanoparticles are involved in the processes of growth and aggregation.

In the present paper we studied the behavior of Cu-57 vol% TiB_2 nanocomposite under conditions of Spark Plasma Sintering (SPS) and conventional sintering.

2. Experimental

2.1. Materials

Titanium (99.5% purity, average particle size 10 μm), amorphous boron (97% purity, average particle size 0.3 μm) and copper (99.7% purity, average particle size 40 μm) were taken as raw powders. Powder mixtures were prepared according to stoichiometry $(Ti + 2{,}1B) + xCu$.

2.2. Preparation of TiB_2-Cu nanocomposites

Ti-B-Cu powder mixtures were mechanically treated for 2–5 min in high-energy planetary ball mill AGO-2 (Institute of Solid State Chemistry and Mechanochemistry SB RAS, Novosibirsk, Russia) 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 pumped and filled with argon. High-energy regimes used (acceleration of balls was 600 ms^{-2}) allowed achieving dramatic changes in the powder mixtures in such a short-duration milling. As it was determined elsewhere [7] combustion rate in SHS-reaction passed through the maximum and decreased to zero with increasing milling time, therefore, prolonged milling was unneeded. Duration of treatment used in the processing corresponded to the maximum in combustion rate. Due to short time of treatment Fe contamination from balls and vials was low (less than 0.5 wt%).

SHS-reaction was carried out in mechanically treated Ti-B-Cu mixtures and was also performed under protective atmosphere. The product of SHS reaction contained submicron TiB_2 particles distributed in copper matrix and was further subjected to subsequent mechanical treatment for 5 min. The size of TiB_2 particles in the resultant product was reduced down to nanolevel. The procedure described above allows obtaining composite powders with high volume content (more than 50 vol%) of titanium diboride particles 30–50 nm in size distributed in copper matrix.

2.3. Conventional sintering

Conventional Sintering was performed on 12 mm diameter tablets of Cu-57 vol%TiB_2 composition prepressed at 400 MPa up to 60–64% green density. Sintering was performed in argon atmosphere at 680 and 950°C, holding time at the maximum temperature was 3 h, heating rate was 10°C/min.

2.4. Spark-plasma sintering

SPS Apparatus (Sumitomo Coal Mining Co., Ltd.) with graphite mold of 10 mm diameter 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 at the maximum temperature was 0–30 min.

2.5. Analysis of microstructure

Microstructure of as-obtained nanocomposite was investigated using Transmission Electron Microscopy (TEM).

To prepare samples for Scanning Electron Microscopy (SEM) studies the compacts were polished and etched with $FeCl_3$-H_2O-ethyl alcohol or $(NH_4)_2S_2O_8$ aqueous solution.

To study the connectivity between titanium diboride particles copper matrix was removed from the surface layer by electrochemical etching in HNO_3-methyl alcohol solution. Microstructure of the compacts was studied by Scanning Electron Microscopy, Energy Dispersive Spectroscopy (EDS) and Electron Probe Microanalysis (EPMA).

3. Results and discussion

3.1. Characterization of nanocomposite powders

Fig. 1 illustrates TEM microstructure of Cu-57 vol% TiB_2 nanocomposite. It is seen that titanium diboride particles are distributed in copper matrix more or less uniformly with local regions containing accumulation of particles. There are also areas where particles form chains. This kind of distribution is believed to favor aggregation under sintering.

3.2. Microstructure of SPS-compacts

Prior to discussion of microstructure of the compacts it should be mentioned that according to X-ray phase analysis no phase changes happened during SPS or conventional sintering.

Spark Plasma Sintering [8] 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

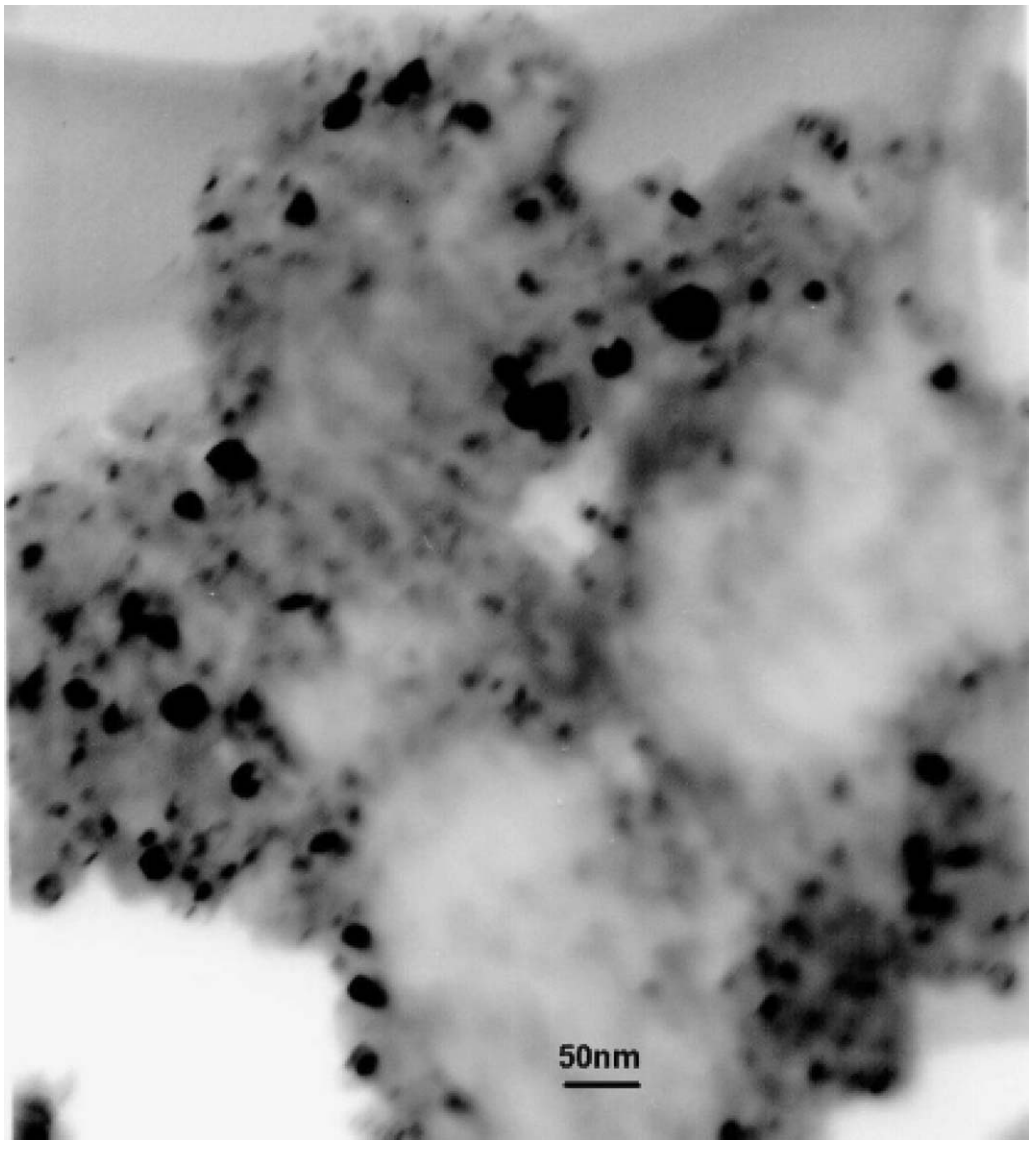


Figure 1 TEM microstructure of Cu-57 vol% TiB_2 nanocomposite.

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.

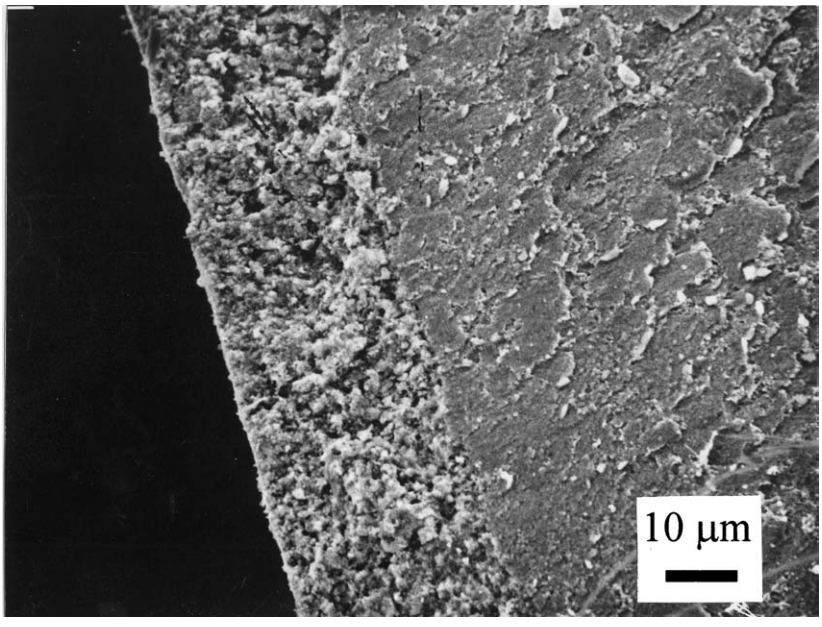
The connectivity between TiB_2 particles was observed when we removed copper matrix from the surface of SPS-compacts by electrochemical etching and formed a layer (Fig. 2a). X-ray phase analysis showed that this layer consisted of titanium diboride. It is seen that the layer has a porous fine-grained 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.

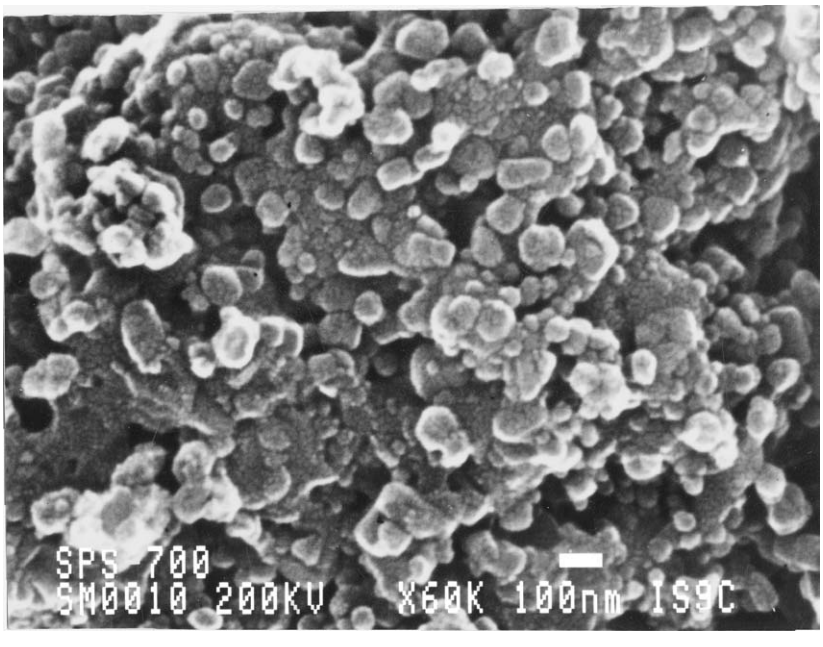
As is seen from Fig. 2b titanium diboride skeleton remains fine-grained with the size of crystallites less then 100 nm. Thus, it can be concluded that peculiarities of SPS compaction is retention of nanostructure in bulk state and formation of titanium diboride skeleton.

In [9] 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 [10]. 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.

Table I demonstrates Vickers hardness of SPS-compacts. Obviously, high hardness values are defined by the presence of TiB_2 skeleton as well as by high degree of densification.



(a)



(b)

Figure 2 (a) Titanium diboride layer revealed on the surface of Cu-57 vol% TiB_2 SPS-compacts after electrochemical etching; (b) nanostructure of the layer.

3.3. Microstructure of conventionally sintered compacts

Conventional sintering of the tablets did not result in densification, green density being retained after sintering. The tablets showed low hardness (Table II). Electrochemical etching of the tablets did not reveal any skeleton, the Cu-depleted layer having weak adhesion to initial material. Thus, no spatial connectivity of TiB_2 particles was obtained by conventional sintering.

It was very interesting to observe formation of fiber-like structures in the samples sintered at 680°C (Fig. 3).

TABLE I Relative density and Vickers hardness (HV) 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

TABLE II Relative density and Vickers hardness of conventionally sintered tablets

Temperature (°C)	Holding time (h)	Green density (%)	Relative density (%)	HV
680	3	60–64	64	94
950	3	60–64	64	178

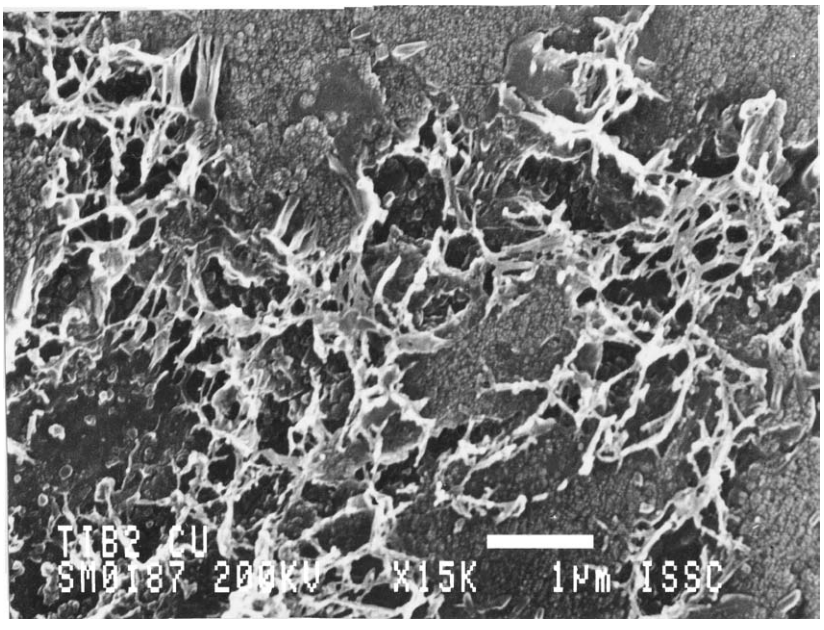


Figure 3 Fiber-like structures of titanium diboride formed during sintering of Cu-57 vol% TiB_2 nanocomposite at 680°C.

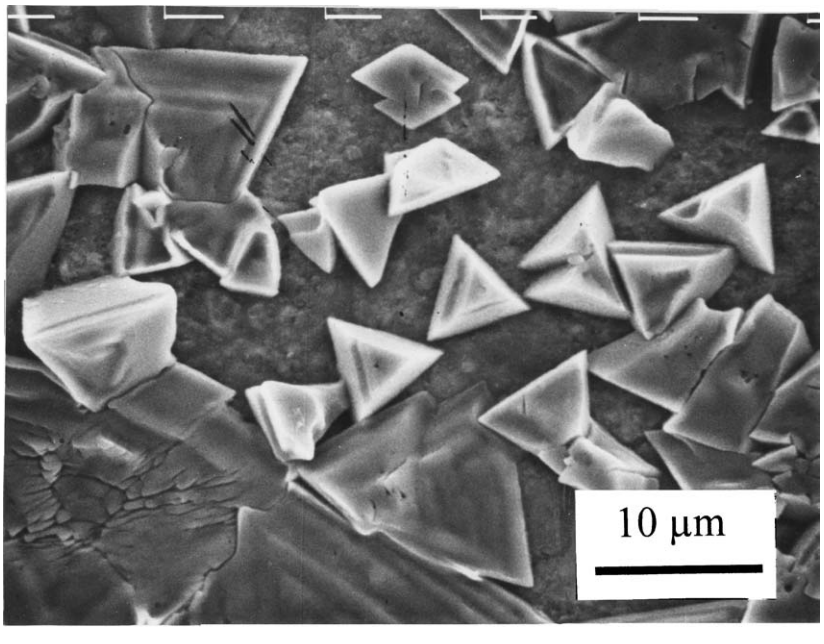


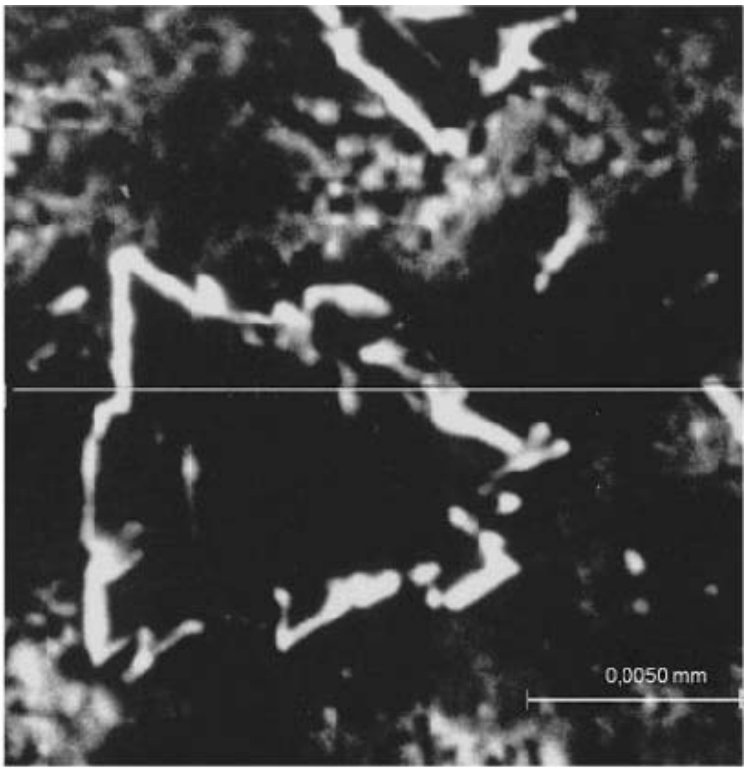
Figure 4 Faceted structures of titanium diboride formed during sintering of Cu-57 vol% TiB_2 nanocomposite at 950°C.

The temperature of sintering is rather low and equal to 0.7 copper melting point and 0.3 titanium diboride melting point. At this temperature diffusion processes in copper matrix are accelerated. It appears that titanium diboride nanoparticles move in solid copper matrix. We assume this moving as an anomalous mass transfer in non-uniform field of stresses.

Non-uniform field of stresses in the composite powders is due to high-energy mechanical treatment used in the synthesis processing. Annealing of vacancies in metal matrix may lead to situations when a plane of matrix at one side of particulate inclusion disappears and appears at the other side [11]. These processes result in moving of the inclusion as a whole. Crystallization by formation of aggregates from nanoparticles is known for systems with liquid as a matrix [12]. It is proposed that so called heterogeneous events in crystallization are favored at high concentrations of solids and low solubility in the matrix. Drawing the analogy to our system, these conditions are satisfied in our case by very low solubility of titanium diboride in copper and by high content of nanoparticles in copper matrix. Association of nanoparticles in aggregates becomes clear when high diffusion activity in dispersed systems and increased sinterbility of nanoparticles are taken into account [13].

The most striking observation was the growth of faceted crystals in the samples sintered at 950°C (Fig. 4). These crystals were analyzed by EPMA line technique (Fig. 5).

Considering the results of X-ray phase analysis and EPMA data it can be concluded that these faceted structures correspond to titanium diboride phase, however, their formation mechanism yet remains unclear.



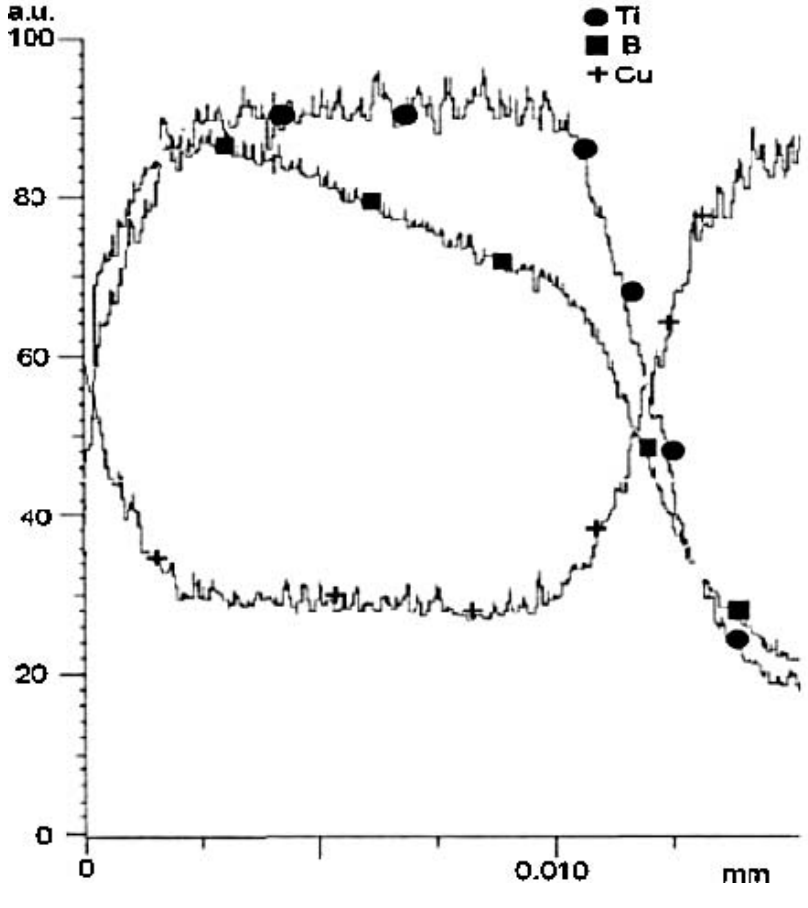


Figure 5 EPMA line analysis for faceted structures.

It is understood that for titanium diboride fiber-like structures and skeleton to be formed in the course of composite microstructure evolution high content of titanium diboride nanoparticles are required. When titanium diboride content is low no connectivity between particles is established and SPS-sintering results in formation of small faceted crystals similar to those obtained in conventionally sintered compacts.

4. Conclusions

The paper focuses on peculiarities of microstructure evolution during sintering of titanium diboride-copper nanocomposites with high volume content of TiB_2 nanoparticles (up to 57%). We have shown that 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.

It was surprising to observe that conventional heating of pre-pressed tablets of the same composition induces formation of shaped structures such as fibers and platelets at low temperatures ($0.7\ T_{m\,Cu}$ and $0.3\ T_{m\,TiB_2}$). Further increase in temperature results in formation of faceted structures. It was proposed that titanium diboride nanoparticles are directly involved in crystallization processes moving as building blocks. This process is favored by high concentrations of particles, low solubility of titanium diboride in copper and high defect concentration in copper matrix stored due to mechanical treatment. A variety of composites with distinctive microstructures can be developed on the basis of this system if evolution of nanostructure of the composite is directed in the way required.

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