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The Cu matrix cermets remarkably strengthened by TiB₂ “in situ” synthesized via self-propagating high temperature synthesis

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Abstract

The TiB₂-Cu cermets with predominant concentration of superhard TiB₂ (from 45 to 90vol.%) were fabricated using elemental powders by means of SHS (self-propagating high-temperature synthesis) process and simultaneously densified by p-HIP (pseudo-isostatic pressing technique). The heat released during highly exothermic SHS reaction was “in situ” utilized for sintering. The combustion occurred even for 50vol.% Cu dilution. According to XRD metallic copper binder was formed in those cermets in whole range of investigated compositions. The TiB₂ volume fraction significantly influenced the properties of fabricated materials, especially grain size and hardness. Both the average grain size and hardness significantly increased with TiB₂ content, so the maximum value of 18GPa was measured for TiB₂-5vol.%Cu composite. Coarse grains of 6.4μm in size were observed for this composite while TiB₂-based submicro-composites were formed for 40-50% of Cu where the average grain size did not exceed 0.6μm. The Vickers hardness of 16-18 GPa obtained for cermets containing from 85 to 90vol.% of TiB₂ and no radial cracks in Vickers hardness test proved that in term of hardness and fracture toughness the composites might be competitive to WC-Co cermets.

Keywords

Titanium diboride,

Copper matrix composites,

Cermets,

self-propagating high temperature synthesis,

Pseudo-hot isostatic pressing,

Hardness

1. Introduction

Due to excellent thermal and electrical conductivity copper based composites are attractive for many applications. Indeed, considerable effort is being devoted to the development of materials with significant copper content [1-7] for applications in petrochemical and electronic industry [4, 6, 8] as well as in aerospace, where the ability to remove heat and retain sufficient strength is of critical importance [9, 10]. Development of such composites with high conductivity and also high strength can be achieved by uniformly distributed ceramic materials such as oxides, borides, carbides and nitrides [2, 4, 5, 11-13] or silicides [14]. Especially TiB_2 , due to extremely high stiffness and hardness (3400HV) [3, 10, 15, 16], ultra-high melting point (3225°C) [3, 17] and the best among borides and carbides both thermal and electrical conductivity (66W/mK) [3, 18] is suitable candidate for Cu-matrix composite [7, 11, 12, 19-21]. Indeed, TiB_2 -Cu cermets formed by dispersion strengthening or precipitation hardening are leading candidates for such applications where an excellent combination of high thermal and electrical conductivity and high-temperature mechanical strength is required [1, 15, 22]. Moreover, TiB_2 is expected to enhance wear, abrasion and erosion resistance in harsh corrosive environments [6, 8, 21, 23]. Such combination of properties makes TiB_2 an attractive precipitant material for copper-based composites applied as electrodes [12], motor brushes and sliding contacts [18, 22] or for marine engineering [24]. On the other hand, predominant ratio of superhard TiB_2 is expected to significantly enhance hardness, and then entirely new applications in cutting tools technologies or precision machinery could be possible [17, 25]. Perhaps, the number of possible applications is much larger, depending on Cu concentration and applied method which both affect the microstructure and the properties of fabricated materials.

Considering phase stability, Cu is the most suitable candidate as a matrix phase for TiB_2 -based cermets. Such elements as Co or Ni which are commercially used in WC sintered carbides technology, are unsuitable as matrix phase for TiB_2 -based cermets, because it was already proven that both nickel and cobalt are unstable in contact with TiB_2 [19, 20]. Contrary to those systems, both high-strength and high-thermal conductivity TiB_2 -reinforced Cu-matrix composites were successfully fabricated [1, 3].

The TiB_2 -Cu wear resistant coatings fabricated by laser technologies [2, 8, 21], or CVD process [24] were reported successful in surface hardening. The Cu-based bulk composites with TiB_2 formed by precipitation or dispersion strengthening were studied several times, using different technologies, sometimes in complex processes, such as ball milling and subsequent annealing [9, 22, 25], hot pressing [18, 23] or hot pressing preceded by mechanical alloying [1, 10], melting and “in situ” synthesis [15], casting process combined with electromagnetic stirring [12], spray forming process combined with melting and hot extrusion [3, 11], pressureless infiltration [23] or melting and gas atomizing [14], sometimes also combined with hot pressing [5]. The combustion synthesis was also applied to fabricate TiB_2 -Cu composites containing 40 wt.% of Cu as described by Xu et al [4]. In order to achieve high strengthening effect, volume ratio of such superhard compound has to be increased. Fabrication of Cu- TiB_2 composites with maximum 70% of TiB_2 by combustion

synthesis was reported by Kwon et al.[26]. However, those researchers were focused rather on bonding with Al core and the hardness of TiB₂-Cu composites was not reported.

The purpose of the present research is to investigate quantitatively the strengthening effect of TiB₂ precipitated in Cu matrix and to supply full characteristics of TiB₂-Cu cermets in wide range of TiB₂ content, from 45 to 90vol.%. Such composites are expected to reveal not only great thermal and electrical conductivity, but also excellent strength, hardness and wear resistance. Since the mechanical properties of composites are determined by size, shape and amount of precipitates, the effect of composition on microstructure refinement is also analyzed, as well as mechanism of fracture, especially in composites exhibiting high hardness. The SHS, proposed in this study, has also some limitations, related to sample size, exothermicity, deviation from adiabatic conditions and concentration of reacting components [27]. Indeed, the effect of significant concentration of diluting Cu (up to 50vol.%) on combustion in SHS, was investigated.

2. Experimental procedure

2.1. Preparation for synthesis

The composites described in this paper were fabricated using commercial elemental powders: Cu (1-5μm, 99.9%, Atlantic Equipment Engineers), amorphous B (0.8μm, 95-97%, Japanese Metal Service), and Ti (45μm, 95%, Osaka Titanium Technologies Co.). In order to complete the B conversion during such rapid SHS reaction, Ti exceeded the amount corresponding to TiB₂ formation, with 5vol.% of Ti-addition excess in the “green compacts”. It means that intended concentration of TiB₂ after SHS corresponded to the range from 45 to 90vol. %. Since TiB₂ was predominant component of investigated composites the samples are referred to as TiB₂-xvol.%Cu, with “x” corresponding to binder content from 5 to 50vol. % respectively. The powders were mixed in Teflon jar, using 2-propanol as a liquid medium, and Ø5mm ZrO₂-milling balls in 40 cycles, (1 minute each) using laboratory planetary mill. The alcohol was partially evaporated on a heating plate at 343K and then the powders were dried for 2h in a vacuum furnace at 573K. Afterward, each powder was pressed in a steel die under a pressure of 550MPa, and then compacts of 30 mm in diameter and 30 mm in thickness were obtained. Fabricated compacts were dried again at the same conditions as those described above. The compacts were covered with a protective graphite sheet, and then inserted into a steel can. Additionally, silicon carbide powder was used in order to separate the compact from the steel can. In order to ensure high vacuum atmosphere inside the experimental device, the air was pumped out from the vacuum chamber for 30min and then can was closed under a pressure of 176MPa in the vacuum chamber.

2.2. The SHS-P-HIP device and process parameters

Samples were simultaneously synthesized and sintered using the SHS-pseudo-HIP method under vacuum of 10 Pa. The steel can containing compact was coiled with heating element and then inserted into a steel die. The scheme of device installed in the press mould was described in the previous paper [19]. Dried sand was used as both a pressing medium and electrical insulator. The mould parts were separated from sand with paperboards, while steel

mould was covered wrapped with a heat-insulating glass wool. The press mould was inserted into a vacuum chamber and put on a pressing machine. The air was pumped out for 1 hour before experiment. Then steel can with sample was heated with a rate of 20K/min, to the ignition temperature of the SHS reaction. The temperature of the bottom of the steel can containing the “green compact” was measured using a type-K thermocouple. The temperature profile during the process is discussed in section 3.1. When the onset of the SHS reaction was detected, pressure was increased from an initial value of 30-35 MPa to 192 MPa and held for 5 min. Samples were taken out after cooling, at least 6 hours after synthesis.

2.3. Characterization of the materials

The phase composition of the investigated composites was determined using XRD technique combined with Rietveld analysis. Both high resolution optical microscopy (Keyence VHX 1000) and FE-EPMA (Jeol JXA-8530F) were applied for microstructure observations; EDS technique was applied in order to confirm the chemical composition of phases distinguished by XRD. The average grain size as well as grain size distribution were determined using planimetric method. The relative density was measured by hydrostatic (Archimedes) method in compliance with ISO 1183-1 [28]. The mechanical properties were evaluated by Vickers hardness tests according to ISO 14705 standard [29], using different diamond indenter load of 300g and 1kg, while for the fracture toughness evaluation high load of 10kg, 30kg and 50kg was also applied. The fracture behavior of the composites was investigated by the microscopic observations of imprints created by diamond indenter during Vickers hardness test. The strengthening effect of TiB_2 on the toughness was evaluated by MOR test, modulus of rupture was determined using Instron 5584. The 4-point bending was carried out with rectangular samples 2.5x5.0x25.0mm with outer span lengths of 21.0mm using crosshead speed of 0.2mm/min, based on the procedure described in [ASTM: C1161 - 02c](#) standard. Testing forces were applied with an electromechanical testing machine with a load capacity of 100kN.

3. Results and discussion

3.1 Exothermic aspects of synthesis

The synthesis of TiB_2 -Cu cermet using the mixture of elemental components was initiated by external heating element and then self-propagated due to highly exothermic reaction involved to TiB_2 combustion synthesis. The onset of the SHS reaction was recognizable by sudden and rapid temperature peak (Fig. 1).

Based on the temperature records it can be assumed that the onset of SHS reaction occurred above 700°C and the maximum temperature of over 1100°C was reached in a few seconds, as is indicated on the derivative curve. Despite the maximum temperature during the process did not exceeded 1200°C, locally several hundred °C higher temperature is expected inside the compact. Such conditions indicated that copper with the melting point of 1080°C was melted when the combustion reaction occurred, and crystallization while cooling. In case of composites the exothermicity depends on composition, so adiabatic temperature decreases, depending on TiB_2 volume fraction, starting from 3190K [19] for 0% of dilution, based on

literature data. When the concentration of TiB_2 is 70, 60 and 50vol.% the adiabatic temperature reaches 2843K, 2652K or 2284K, respectively [26]. However, the adiabatic temperature describes the maximum temperature for adiabatic conditions, which cannot be ensured in the experimental device, especially when applying high pressure simultaneously with the combustion synthesis, indeed the temperature during synthesis measured in the steel can covering reacting compact was much lower than theoretical one. Based on the temperature records it can be assumed that the synthesis of TiB_2 -Cu composites can be carried out in relatively simple device despite extremely high exothermicity of TiB_2 synthesis.

3.2 Phase composition and microstructure

According to XRD pattern, only two phases (TiB_2 and elemental Cu metal binder) were proved in each sample (Fig. 2).

Such data is consistent with the results reported by Dudina et al.[6] who fabricated similar composites by high energy mechanical milling, other investigations on combustion synthesized TiB_2 -Cu composites reported by Xu et al.[4], as well as thermodynamic calculations. The amount of Cu depended on the content in the “green sample”. None of unfavorable binary compounds, i.e. Cu_3Ti , reported by Y. J. Kwon et al.[26], were detected in those materials. Contrary to reference investigations, fine boron precursor was used in this study (amorphous boron $0.8\mu\text{m}$), which could be useful in reaction completeness. If the reaction of Ti with boron is uncompleted, titanium may react with Cu and form intermetallic binder. Therefore, the specific area of non-metallic precursor determining whether the process can proceed with high efficiency is of significant importance for carbides or borides synthesis by means of SHS. Due to high melting point of boron (2300°C), formation of boride involves reaction with Ti which is initiated on the surface of boron grains. Such reaction which results in TiB or TiB_2 formation is strongly exothermic, therefore the heat released from the product is used in turn in order to propagate the SHS reaction. It is expected that finer boron precursor can ensure not only higher contact area when the process starts but also high efficiency synthesis of TiB_2 when boron is soluble in partially melted metal (Ti, Cu). Similar effect of precursor grain size on the reaction effectiveness was discussed in the previous study [30]. The average grain size of Ti precursor is not as important, as for high melting point B, because in this case, unreacted Ti melts due to heat released from highly exothermic reaction. However, broadening of peak in position 2θ about 42° observed for materials with 40 and 50vol.% of Cu may indicate that small amount of Ti was soluble in Cu matrix. The 6wt.% solubility of Ti in Cu is possible, according to phase equilibrium diagram [31]. The Rietveld method analysis combined with XRD pattern revealed 2% of $\text{Cu}_{0.97}\text{Ti}_{0.03}$ for sample with content of TiB_2 reduced to 45vol.%. Such small concentration (2vol.%) is very close to XRD detection limit. This is why such compound could not be detected in samples with smaller Cu content. It can be also observed that intensity of main peaks originated from Cu do not increase linearly with the Cu content in the composites. That effect is especially visible for the range of 30-60 vol.% of TiB_2 . However, it has to be considered that not only the chemical composition, but also the grain size of crystallites determines the intensity in XRD pattern. That effect is fully justified, because broadened peaks are observed on the pattern corresponding to sample containing the highest concentration of Cu matrix. Therefore, small

size Cu crystallites are expected for this composite. This result meets the expectations, since formation of TiB_2 diluted by significant amount of Cu caused significantly reduced heat effect, which resulted in very limited grain growth while cooling down.

The concentration of TiB_2 influenced significantly the densification (Fig. 3), as well as the grain size (Fig. 4). Considering the relative density, best effect of densification was achieved for the composites with 65-75% of TiB_2 , because the relative density is very close to that of theoretical one. The porosity increased to 6-8% when the TiB_2 content increased to 85-90vol% of TiB_2 , as well as when the amount of TiB_2 was significantly reduced to 55-60vol%.

The data of relative density are approximately consistent with the observed microstructure (Fig. 4). Darker phase corresponds to TiB_2 while the Cu forms light gray matrix. Since the relative density is very high, almost no porosity is observed, especially in composites with fine grains in the microstructure.

Small porosity can be observed in the composites containing very high concentration of TiB_2 (80-90vol.%) and the pores look like small black inclusions, especially on the TiB_2 -matrix interface. Such porosity could not be avoided while employing “in situ” reaction combined with densification by HIP. Contrary to conventional techniques of densification, SHS is short term process, where the reaction is initiated, propagated in several seconds. After the process, the temperature decreases and then additional densification does not occur. It has to be emphasized that in situ reaction of raw elemental powders involves significant volume contraction, as a result causes shrinkage of compact. In order to express it more quantitatively, simple calculation is needed. In order to fabricate 1 mole of TiB_2 1 mole of elemental Ti and 2 moles of B are needed. The overall volume of elemental powders mixture occupies 10.543cm^3 of Ti, and 9.24cm^3 of B, which totally occupies $19,783\text{cm}^3$. Finally, 1 mole of TiB_2 is formed which occupies $69.489/4.52=15.374\text{cm}^3$. Therefore, the contraction originated from synthesis is about 22.3vol.%. Considering that the relative density of raw compact is about 60vol.% and compact contains about 40vol.% of porosity, overall densification of material consisting only of Ti and B during SHS reaction should be more that 60vol.%. Such shrinkage should be compensated by the external pressure (HIP). Based on the results, such volume contraction is sufficient when the concentration of metal binder is enough to avoid necking between TiB_2 grains.. Indeed, metal binder is necessary to simplify the mass transport, reduce friction, especially when melting of the binder occurs. Moreover, metal binder plays a role of inert filler and reduces the SHS rate as well as maximum temperature while the reaction is propagated (by heat consumption utilized for melting). However, negligible concentration of binder metal causes that SHS rate is too rapid, and TiB_2 grains contain more defects, including closed porosity, caused by thermal expansion coefficient at high temperature when the grains are formed and then cooled down. The reaction mechanism is expected to be modified, depending on TiB_2 :Cu ratio in the final composite. Depending on many factors, such as reacting ingredients grain size, TiB_2 :Cu ratio, compact size and adiabaticity, different maximum temperature and different amount of liquid phase is formed. It can be assumed that the reaction is a combination of solid state reaction of Ti with B in the initial stage of the process, melting of Cu and partially Ti, some solubility of unreacted in the liquid phase and recrystallization. As a result, good densification can be obtained especially when sufficient

volume fraction of Cu binder was applied. The porosity in composites characterized by significantly high concentration of TiB_2 (more than 75vol%) is difficult to be avoided by using “in situ” SHS process. On the other hand, high temperature is required for melting of Cu and good densification. Therefore, the composite having 45vol% of TiB_2 exhibited significantly reduced relative density. That means the overall heat released from the TiB_2 formation was not enough despite the mechanism of plastic deformation.

The investigations on the grain size distribution indicated that the average grain size is reduced significantly with decreasing TiB_2 content. The relatively coarse grains with several micrometers in size were observed on the microstructure with 80-90vol% of TiB_2 while ultrafine grains with average grain less than $0.6\mu\text{m}$ in size were obtained for composites when Cu matrix content increased to 50-60vol.% (Fig. 5).

The grain size distribution was also affected by Cu content (Fig. 6), starting from monomodal distribution for 5vol.% of Cu, to significantly predominant ratio of the smallest in size TiB_2 grains.

The effect of grain growth in the composites having significantly predominant volume fraction of TiB_2 can be explained by Ostwald ripening process. The concentration of TiB_2 affects the maximum temperature in the reacting compact directly after combustion by means of SHS process occurred. When the concentration of TiB_2 is high and only negligible amount of diluting Cu exists, maximum temperature increases. As a result, better conditions for such processes, as dissolution of small size high energy grains which can precipitate on the bigger ones, are ensured. Therefore, the tendency to reduce free energy causes large precipitates to grow, drawing material from the smaller precipitates. Such process occurs because larger grains are more energetically stable than smaller particles. The significant differences in the microstructure are confirmed by the SEM microstructure with higher magnification (Fig. 7)

The size of precipitated grains exhibited good conformance with references. Kwon et al.[26] reported grains of less than $4\mu\text{m}$ in size formed in situ by the combustion reaction for composites containing 60vol.% of TiB_2 , however refined grains could be observed in those microstructures.

3.3 Hardness and modulus of rupture

Since the Vickers hardness for pure Cu is lower than 1.0 GPa [9, 15, 22, 31], great strengthening effect was proven for TiB_2 -based Cu matrix composites. (Fig. 8).

The Vickers hardness indentation was carried out for each investigated composite under room temperature for 15 seconds, in two series under loads of 0.3 and 1.0kg, in order to compare the results directly. The Vickers microhardness slightly higher than hardness confirmed good homogeneity and low porosity of investigated composites. The hardness of 6-8 GPa and small spread of results confirmed by low standard deviation was achieved for samples with TiB_2 concentration in the range of 45-75vol.%. These results may be explained by relatively high content of plastic Cu matrix and small interaction between TiB_2 grains. It is worth of emphasizing that increased concentration of TiB_2 caused extraordinarily improved hardness,

which reached maximum value of 16-18GPa for 85-90vol.% of TiB_2 . Such results revealed good compliance with expectations, because theoretically extremely high Vickers hardness of 34GPa should be expected for pure nonporous monophase TiB_2 [3]. Considering the Vickers hardness it can be assumed that the materials with the binder phase in the range of 5-15vol.% are comparable or even better than WC-Co composites with similar (6-10vol%) concentration of binder despite coarse grains and softer binder. Richter and Ruthendorf [32] investigated the effect of grain size on the hardness of WC-Co and the maximum hardness of 1500-1650HV could be obtained only for fine (0.8-0.95 μm) grain size in the microstructure while the hardness decreased to 1150 – 1100HV when the coarse grains (3-6 μm) were obtained. It means that in the present research remarkable effect of ultra-hard TiB_2 is revealed in such cermets.

Based on Vickers hardness indentation the mechanism of cracks formation can be assumed. Essentially neither the lateral and radial (Palmqvist) cracks nor median (half-penny) cracks [33], which are expected for brittle covalent ceramics, were observed (Fig. 9).

These microstructures indicate that the composites revealed rather plastic than brittle behavior, caused by plastic deformation of Cu-matrix. The shape of deformed zone around the Vickers imprint corresponds to the zone observed in pure copper (Fig. 9D) in each composite, while the radius of deformed composites decreased with increasing concentration of strengthening TiB_2 . The composite with 50vol.% of Cu exhibited relatively low hardness, so the plastic deformation during hardness test was significant. Due to strengthening the ductility of TiB_2 -Cu composite is expected to be reduced comparing to pure metallic Cu [3, 15]. Indeed, round shape cracks appeared around imprint caused by Vickers indenter (Fig. 9C). Moreover, several radial cracks were formed under load of 50kg in the composite containing 15 vol.% of Cu (Fig. 9A). Such behavior is predictable, because when applying high load during indentation Palmqvist cracks are formed for cermets, such as WC-6wt.%Co. Since only few short cracks appeared, originating just from one corner such materials are still considered as reasonably-tough, based on Niihara et al theory [33], and this behavior indicates cermets with high fracture toughness.

The results of bending test revealed, that the strongest strengthening effect by TiB_2 grains on Cu matrix expressed by modulus of rapture was obtained for the composite having 65vol.% of TiB_2 (Fig. 10).

Contemporary cemented carbides based on WC-Co are non-porous and characterized by fine or ultra-fine microstructure, indeed high modulus of rapture can be obtained [34, 35]. However, considering preliminary results for relatively large samples of WC-Co cermets having coarse grains and elevated Co content, similar to those reported in this study (1000-1500MPa) were reported [36]. Apparently better results should be obtained in this research by using 3-point bending technique. Modulus of rapture measured by 4-point bending test is always more severe than that of 3-point bending, so the results are difficult to be compared directly.

The modulus of rapture vs. TiB_2 vol.% relationship revealed good compliance with relative density. Such effect meets the expectation when considering Weibull theory. As the deviation

from theoretical density increases, the modulus of rupture decreases dramatically, since the modulus of rupture is strongly affected by any defects in the microstructure.

Since the overall porosity, its distribution and geometry determine the brittleness, small grain size composites with entirely reduced porosity are required in order to ensure satisfactory high modulus of rupture. That means the composites with TiB_2 volume fraction of more than 80vol.% of TiB_2 should be fabricated using more conventional sintering technics (HP, HIP, or SPS) in order to control the grain size, their distribution and to eliminate porosity. The further studies on TiB_2 -Cu cermets are fully justified since the investigated composites with high TiB_2 content exhibited high hardness, despite some porosity and coarse grains.

4. Conclusions

Based on the experimental results obtained for TiB_2 -Cu cermets fabricated by SHS following conclusions can be drawn:

1. The SHS-p-HIP method revealed to be sufficient in order to fabricate TiB_2 -Cu cermets with broad range of diluting Cu, from 5 to 50vol.%. Despite non-adiabatic conditions, combustion caused by TiB_2 exothermic synthesis occurred, even for 50vol.% of diluting Cu. Each composite exhibited high relative density, especially those containing at least 15vol.% of matrix phase.
2. Regardless of the negligible solubility of Ti in Cu matrix which is recognizable by XRD as $\text{Cu}_{0.97}\text{Ti}_{0.03}$, only two phases, Cu and TiB_2 , were detected based on structural analysis. It means that elemental Cu is thermodynamically stable binder for TiB_2 based cermets,
3. The effect of Cu concentration was proved in term of microstructure and hardness. The increased binder content caused reduction of TiB_2 grain size, however hardness significantly decreased when the concentration of Cu exceeded 15vol.%.
4. Considering relative density and modulus of rupture (over 1500MPa) the best properties exhibited composite having 65vol.% of TiB_2 .
5. The maximum hardness of 16-18GPa for samples with the lowest concentration of Cu (5-10vol.%) may indicate that TiB_2 -based composites with Cu binder could be competitive to commercially used WC-Co cermets, despite soft metallic Cu used as the matrix. However, low modulus of rupture for such hardest composites indicates that coarse grains and porosity deteriorated the bending strength significantly. Therefore, further study on the TiB_2 -Cu cermets using conventional sintering methods is of significant importance in order to take full advantage of their remarkable hardness.

References

- [1] S. J. Dong, Y. Zhou, Y. W. Shi, B. H. Chang, Formation of a TiB_2 -reinforced copper-based composite by mechanical alloying and Hot Pressing, *Metall. Mater. Trans. A*, 2002; 33A:1275-80
- [2] L. Y. Gu, G. Y. Liang and Z. B. Zheng, Investigation of in situ Cu- TiB_2 composite on the copper using later melting synthesis, *J. Mater. Eng. Perform.* 2007; 16 (5): 54-8

- [3] Jongsang Lee, Nack J. Kim, The influence of reinforced particle fracture on strengthening of spray formed Cu-TiB₂ composite, *Scr. Mater.*, 1998;39, 8: 1063-9
- [4] Qiang Xu, Xinghong Zhang, Jiecai Han, Xiaodong He, V. L. Kvanin, Combustion synthesis and densification of titanium diboride-copper matrix composite, *Mater. Lett.* 2003;57:4439-44
- [5] D. Bozic, I. Cvijovic-Alagic, B. Dimcic, J. Stasic, V. Rajkovic, In-situ processing of TiB₂ nanoparticle-reinforced copper matrix composites, *Science of Sintering* 2009;41:143-50
- [6] D. V. Dudina, V. I. Mali, A. G. Anisimov, O. I. Lomovsky, Shock compression of Ti-B-Cu powder mixtures: Microstructural aspects, *Mater. Sci. Eng., A* 2009;503:41-4
- [7] J. Ruzic, J. Stasic, V. Rajkovic, D. Bozic, Strengthening effect in precipitation and dispersion hardened powder metallurgy copper alloys, *Mater Design* 2013;49:746-54
- [8] J. Dutta Majumdar, B. Ramesh Chandra, D. Biswas, B. L. Mordike, I. Manna, In situ dispersion of titanium boride on copper by laser composite surfacing for improved wear resistance, *Lasers in Eng.*, 2006;16:333-48
- [9] C. Biselli, D. G. Morris, N. Randall, Mechanical alloying of high-strength copper alloys containing TiB₂ and Al₂O₃ dispersoid particles, *Scr. Metall. Mater.*, 1994; 30(10):1327-32
- [10] Z. Y. Ma, S. C. Tjong, High temperature creep behaviour of in-situ TiB₂ particulate reinforced copper-based composite, *Mater. Sci. Eng.* 2000;A284:70-6
- [11] Jongsang Lee, J. Y. Jung, Eon-Sik Lee, W. J. Park, S. Ahn, Nack J. Kim, Microstructure and properties of titanium boride dispersed Cu alloys fabricated by spray forming, *Mater. Sci. Eng., A* 2000;277:274-83
- [12] T. K. Jung, S.C. Lim, H. C. Kwon, M. S. Kim, Fabrication and properties of TiB₂ reinforced Cu composites by electromagnetic stirring, *Mater. Sci. Forum*, 2004;449-452:297-300
- [13] H. B. M. Rajan, S. Ramabalan, I. Dinaharan, S. J. Vijay, Synthesis and characterization of in situ formed titanium diboride particulate reinforced AA7075 aluminum alloy cast composites, *Mater Design* 2013;44:438-45
- [14] D. Bozic, M. Mitkov, M. T. Jovanovic, Structure and Microhardness of precipitation/dispersion hardened Cu-Ti-B and Cu-Ti-Si alloys, *Mater. Charact.* 1994;32:97-103
- [15] J. P. Tu, N. Y. Wang, Y. Z. Yang, W. X. Qi, F. Liu, X. B. Zhang, H. M. Lu, M. S. Liu, *Mater. Lett.* 2002;52:448-52
- [16] Y. Zhang, N. Ma, H. Wang, Y. Le, X. Li, Damping capacity of in situ TiB₂ particulates reinforced aluminium composites with Ti addition, *Mater Design* 2007;28:628-32

- [17] J. Song, Ch. Huang, B. Zou, H. Liu, J. Wang, Microstructure and mechanical properties of TiB₂-TiC-WC composite ceramic tool materials, *Mater Design* 2012;36:69-74
- [18] P. Yih, D. D. L. Chung, Titanium diboride copper-matrix composites, *J. Mater. Sci.* 1997;32:1703-9
- [19] Marta Ziemnicka-Sylwester, Kiyotaka Matsuura, Munekazu Ohno, Phase evolution, microstructure and hardness of TiB₂-based Co-containing composite by SHS under pseudo-isostatic pressure, *ISIJ Int.* 2012;52(9):1698-704
- [20] Marta Ziemnicka-Sylwester, Superhard TiB₂-based composites with different matrix fabricated from elemental powders by SHS-p-HIP, *Adv. Sci. Technol.*, 2013; 77:146-52
- [21] Xue Liu, Sen Yang, In situ TiB₂ particles reinforced copper matrix composite coating on mould steel by laser cladding, *Mater. Sci. Forum*, 2010;654-656:1856-9
- [22] S. C. Tjong, K. C. Lau, Abrasive wear of TiB₂ particle-reinforced copper matrix composites, *Mater. Sci. Eng., A* 2000;282:183-6
- [23] J. Lu, S. Shu, F. Qiu, Y. Wang, Q. Jiang, Compression properties and abrasive wear behavior of high volume fraction TiC_x-TiB₂/Cu composites fabricated by combustion synthesis and hot press consolidation, *Mater Design* 2012;40:157-62
- [24] Seiji Motojima, Hiroaki Kosaki, Resistivities against sea-water corrosion and sea-sands abrasion of TiB₂-coated copper plate, *J. Mater. Sci. Lett.* 1984;4:1350-2
- [25] P. C. Cobb, Technical Report Titanium Carbide as a sintering agent for titanium boride, *Mater Design* 1990;11:156-9
- [26] Y. J. Kwon, M. Kobashi, T. Choh, N. Kanetake, *Scr. Mater.* 2004;50:577-81
- [27] V. I. Itin, A. D. Bratchikov, A. G. Merzhanov, V. M. Maslov, Principles of Self-Propagating High-Temperature Synthesis of Titanium Compounds with Elements of the Iron Group, *Combustion, Explosion and Shock Waves*, 1981;17(3): 293-8
- [28] ISO 1183-1:2012(E). Plastics - methods for determining the density of non-cellular plastics - Part 1: immersion method, liquid pycnometer method and titration method. Geneva, Switzerland. p. 1-17.
- [29] ISO 14705:2008(E) Fine ceramics (advanced ceramics, advanced technical ceramics) — Test method for hardness of monolithic ceramics at room temperature, p. 3-17
- [30] M. Ziemnicka-Sylwester, TiB₂-based composites for ultra-high-temperature devices, fabricated by SHS combining strong and weak exothermic reactions, *Materials* 2013;6:1903-19
- [31] H. Baker. H. Okamoto, Alloy phase diagrams, ASM Handbook, volume 3, ASM International, 1992, 775-7

- [32] V. Richter, M. V. Rathendorf, On hardness and toughness of ultrafine and nanocrystalline hard materials: *Int. J. Refract. Met. Hard Mater.* 1999;17:141-52
- [33] K. Niihara, R. Morena, D. P. H. Hasselman, Evaluation of K_{IC} of brittle solids by the indentation method with low-crack-to-indent ratios, *J. Mater. Sci. Lett.* 1982;1:13-6
- [34] T. Klunsner, S. Wurster, P. Supancic, R. Ebner, M. Jenko, J. Glatzle, A. Puschel, R. Pippan, Effect of specimen size on the tensile strength of WC-Co hard metal, *Acta Mater.* 2011;59:4244-52
- [35] S. Zhao, X. Song, Ch. Wei, L. Zhang, X. Liu, J. Zhang, Effect of WC particle size on densification and properties of spark plasma sintered WC-Co cermet, *Int. J. Refract. Met. H.* 2009;27:1014-8
- [36] S. Okamoto, Y. Nakazono, K. Otsuka, Y. Shimoitani, J. Takada, Mechanical properties of WC/Co cemented carbide with larger WC grain size, *Mat Char*, 2005;55:281-7

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