

Article

Vaporization and Poor Wettability as the Main Challenges in Fabrication of TiB₂-Cu Cermets Studied by SPS

Marta Ziemnicka-Sylwester

Division of Materials Science and Engineering, Hokkaido University, Kita 13 Nishi 8, 060-8628 Sapporo, Japan; E-Mail: marta.zs@eng.hokudai.ac.jp; Tel./Fax: +81-11-706-6345

External Editor: Hugo Lopez

Received: 31 October 2014; in revised form: 9 December 2014 / Accepted: 11 December 2014 / Published: 19 December 2014

Abstract: TiB₂-Cu cermets with various volume fractions of copper (from 3 to 30 vol. %) were produced via liquid phase sintering at the temperature range 1100–1200 °C in vacuum using spark plasma sintering (SPS) technique. Full densification could not be achieved as the consequence of poor wettability and vaporizing Cu. The quantitative Rietveld analysis indicated that insignificant reduction in Cu content occurred only in sample with initially 3 vol. % of Cu, but then densification was negligible. The relative density improved along with increasing volume content of Cu (10–20 vol. %), but then predominant amount of Cu introduced was reduced as the effect of vaporization or swelling, which caused that pellet with intended 20 or 30 vol. % of Cu contained respectively only 6 or 17 vol. % after sintering. Moreover, Cu droplets were released from the die at the temperature of 1000–1030 °C near the Cu melting point. The effect of vaporization was successfully reduced by increased heating rate and when isothermal annealing process was skipped, however, it could not be entirely eliminated. The experimental results on Cu vaporization are confronted with parameters that are commonly considered in the production of cermets, such as oxidation, wettability, contact angle and viscosity as well as their impact on densification.

Keywords: cermets; vaporization; wettability; TiB₂; MMCs; SPS; liquid phase sintering; rietveld method

1. Introduction

1.1. *TiB₂-Cu Cermets Produced by Liquid Phase Sintering Using Spark Plasma Sintering (SPS)*

Metallic Cu is a superior electrical conductor [1] with broad applicability in electronics and electric circuits due to both extraordinarily high thermal and electrical conductivity [2,3]. However, it is a relatively soft metal, thus hardening by alloying elements is widely applied [4]. On the other hand, coarse precipitates that are formed at high temperatures may deteriorate both conductivity and mechanical properties. Therefore, high thermal stability strengthening dispersive, typically refractory oxides, borides or carbides [3,5], are required to extend the lifetime of electrodes or other Cu-matrix composites working at high temperature [2].

TiB₂ especially is a great candidate for copper reinforcement, because due to high thermal and electrical conductivity [6], the effect of deteriorating electrical conductivity of copper is much lower than when other ceramic particles are used [4]. Such metal-like compound also has a very high melting point of 3225 °C [7,8]. The combination of the above-mentioned properties makes TiB₂-Cu cermets potentially great candidates for applications where good electrical and/or thermal conductivity is needed [4,5]. For many systems, the fabrication of cermets is impossible, due to thermodynamic aspects. For instance, formation of intermetallics at elevated temperature occurs in many systems. Compared to those systems, Cu is a thermodynamically stable binder for TiB₂, and intermetallics can be entirely avoided [9], which makes the boride a unique candidate for strengthening of the Cu matrix. Due to the application of very hard TiB₂, hardness, strength, as well as wear and erosion resistance can be significantly improved. By using high volume fraction of TiB₂ even the application in cutting tools technology is possible [3,10,11] because remarkably hard cermets can be obtained [7–11].

However, both good mechanical properties and high thermal conductivity of composites require excellent bonding, and eliminating porosity entirely. Therefore, search for effective sintering techniques is a fully justified challenge to be undertaken. Such systems were studied and already reported in several papers [3–5,9,10,12], including sintering by SPS, and the results were consistently confirmed. Also compaction of Cu or Cu-based powder mixtures by means of SPS technique has been studied at least several times, using different grain size powders and various sintering conditions [2,13,14].

The SPS technique is recently considered as very attractive method to produce cermets [12], which is caused by its unique combination of parameters, such as essentially short sintering time [3,14], resistive heating of the sintered powder with an electrical current and simultaneous uniaxial pressure [2,12,13]. Such conditions are favorable, especially in the technology of nanocomposites, because the grain growth is strongly limited by short sintering time [12,14]. Thanks to a strong electrical current, the liquid phase can be easier generated. If only the solid ceramic particles were wettable by the liquid metal, high relative density could be achieved rapidly in a short process [2]. Indeed, SPS was the densification technique used in this study.

1.2. *Wettability and Contact Angle*

It is a well-known phenomenon that much better densification can be obtained if the sintered material is wettable by the liquid made of sintering additive. A solid material is considered wettable if the contact angle equals less than 90°. Most papers published on wettability, viscosity issues, as well as capillary

forces are focused on theoretical approaches, while the experimental data for wettability of solids by molten metals, including copper are rather limited to several papers, mostly applying the model of sessile drop method.

Polycrystalline TiB_2 is wettable by liquid aluminum [6,15], which makes the TiB_2 -Al system of practical application in Hall-Heroult cell. Reference data on the TiB_2 -Cu system indicate lack of wettability, because the contact angle is large and characterized by huge spread of values, 130° , 140° – 142° [6,16], or even 158° [12]. In such case the liquid phase would rather evaporate or leak out from the SPS die under high pressure, than eliminate porosity. Such scenario was previously mentioned by Biswas [12] where the scenario of non-wetting liquid was clearly explained. If during the liquid-phase sintering, there is a chance of transition of this angle from less than 90° to the non-wettable range with contact angle of more than 90° , the liquid formed will start to uncover the solid phase. Alternatively, the liquid may move out of the powder compact as a result of mechanical pressure in SPS, thereby creating porosity and a concomitant decrease in density.

Actually, the results on contact angle between Cu-based alloys modified by titanium with increasing temperature presented by Nicholas *et al.* [17] indicated clearly that contact angle can essentially be reduced with increasing temperature. Therefore, the scenario of transition from wettable to non-wettable contact angle with increasing temperature in sintering process is rather not expected, but the real value of contact angle in TiB_2 -Cu system is difficult to be measured with good accuracy, considering purity of components used as well as pressure as important parameters.

Biswas *et al.* [12] have proven that TiB_2 revealed deteriorating effect on the densification of copper, while a Pb addition can improve sintering ability of copper because of the low melting point of Pb (227°C). Another successful approach to improve the wettability of TiB_2 was by using the combined (Cu, Ni) liquid phase for cermets, since Ni wets TiB_2 [6]. However, other studies revealed that contact of TiB_2 with molten nickel brought about extensive corrosion with formation of Ti-Ni secondary phases [18]. Such formation of Ti-Ni intermetallics is consistent with the previous results of the present author [19]. However, a small amount of Ti is most likely an effective method in reduction of the contact angle for TiB_2 -Cu melt system [18].

The results on Cu-matrix composites via liquid phase sintering studied for W-Cu system indicated that a modification of matrix by lead Pb, Ni or Co is an effective method to improve wettability in liquid phase sintering process when copper is used as the liquid metal [20]. However, such additional components affect also the melting point and ductility of the matrix, especially when formation of intermetallic phases is possible [19]. Aizenshtein with co-authors [21] measured the contact angle in $(\text{B}_4\text{C} + \text{TiB}_2)/\text{Cu}$ system to be approximately 55° and it could be successively reduced to approximately 15° – 20° by 16 at.% of boron addition. Thus, theoretically, if any solubility of TiB_2 in Cu would occur, such effect is expected to improve wettability.

1.3. Capillary Forces

Capillary forces are the most significant mechanism responsible for agglomeration, rearrangement stage and affect densification in liquid phase sintering. This phenomenon is difficult to be measured, so a theoretical approach is used more often, taking into consideration among others particle size, contact angle, distance between particles and liquid volume [22–24]. A significant fraction of pores can be filled

by the liquid film within a very short time due to the capillary forces for systems with wettable liquids. However, at large contact angles and intermediate particle separation, capillary forces equal to zero should be expected [22]. Actually, the distribution of ceramic grains in the powder or pellet exposed to sintering is entirely random, and ceramic powders are characterized by typically monomodal grain size distribution. Therefore, it should be taken into consideration that the theoretical dissertations provide only a model for ideal rearrangement and almost continuous transition from bridge to direct contacts while sintering, which cannot be realized experimentally. Experimental approach to the rearrangement process in liquid phase sintering was presented by Huppman and Riegger [25] who used planar arrays of uniform size copper-coated tungsten in order to compare directly those liquid phase sintered samples with the pre-sintered one. The research focused on particle rearrangement for various liquid phase ratio, contact angle and packing density. Based on those parameters they assumed that shrinkage by rearrangement occurs in randomly packed arrays and it is in direct relation to the capillary forces produced by the inter-particle liquid bridges. Xu and Mehrabadi [24] confirmed the assumption that viscous flow within the liquid bridges and the relative sliding of particles, which is called grains rearrangement, bring about densification in the initial stage of the liquid phase sintering. Huppman and Riegger [25] also found that increased sintering time does not actually affect further rearrangement process, so significant shrinkage occurs only in the initial stage of liquid phase sintering until direct contact between solid grains occurs. But under conditions of poor wetting capillary forces may become repelling, which results in swelling [25]. Capillary forces could be strong only for small size of channels. It could be expected that small capillary forces may be partially compensated by external uniaxial high pressure used in the present experiments. However, the actual impact of such high pressure on grains rearrangement when capillary forces are weak in TiB₂-Cu system is unknown, so it will be investigated in the present study.

1.4. Effect of Contaminations on the Densification of TiB₂

Carbon and oxygen are the most common impurities in the technology of so called non-oxide ceramics bulk materials.

The effect of carbon, which usually originates from graphite mold in HP and SPS, or is intentionally applied as the sintering additive, is rather beneficial than deteriorating for sintering. It has already been proven for many systems that sintering ability of high temperature materials, such as TiB₂, can be significantly improved by increased sintering temperature. However, graphite die may start to dissolve or even react with sintered material when the densification process is carried out at significantly high temperatures. Most likely, Venkateswaran *et al.* [10] faced this problem while sintering TiB₂-6 vol. % Cu at 1550 °C by SPS. Authors observed improved sintering ability with increasing temperature up to 1550 °C. Scientific evidence of that assumption could be an extraordinary and rather broadened peak for the diffraction angle of $2\theta = 27^\circ$, so much higher intensity than expected for TiB₂ was observed in the X-ray diffraction (XRD) pattern. Also the fact that increasing holding time brought about higher relative density when sintering was carried out at 1500 °C while such effect of sintering time was not observed at 1400 °C may indicate solubility of carbon at 1500 °C. Moreover, significantly lower than expected hardness (17 GPa) was reported in that study.

It is a well-known problem for sintering of non-oxide ceramics, such as carbides or borides, that oxide contaminations deteriorate sintering ability. However, that whole effect should be analyzed with the consideration to the sintering mechanism. For instance, when liquid phase sintering is applied (the case of TiB₂-Cu cermets), densification process will be affected by wettability of TiO₂, B₂O₃, or Cu₂O compared to that in a pure TiB₂-Cu system. As the result of limited wettability, residual porosity cannot be eliminated and the mechanical properties are essentially deteriorated.

The second aspect of oxygen contaminations in consolidation can be most likely attributed to the strong impact on the vapor-phase transport kinetics mechanism. Both TiO₂ and B₂O₃ possess much lower melting point than TiB₂ (1870 °C, 500 °C and 3225 °C, respectively). Evaporation of boron oxide is intensive in the temperature range from 1400 to 1600 °C [26], which is potentially the right temperature for cermets production.

Taking into consideration low temperature of consolidation, the effect of oxide impurities on the sintering ability of Cu was also the subject of reported studies at 600 °C [13] when intentionally oxidized Cu seemed not to have marked effect on the SPS consolidation process. The reasons of such behavior can be attributed to similar melting point of Cu and its oxide (1083 °C and 1220 °C, respectively), or good wettability of Cu₂O by liquid copper.

1.5. Chemical Stability and Vaporization of Copper

Metallic Cu is a rather chemically inert material; however it possesses relatively low thermal stability. Essential vapor pressure can be generated when copper is exposed to elevated temperature or electric field. The effect of vaporizing Cu was recently discussed in several papers [1,27]. For instance, Lee with co-workers [27] deposited copper thin films by thermal evaporation at 1300 °C. They were able to obtain 120 nm thick coatings within 5 min on charged substrates at the temperature just slightly higher than the densification temperature applied in this study. Apparently similar conditions are common in sintering process, especially in SPS, where huge charge is applied, so it can be assumed that such conditions can also be favorable for vaporization of Cu powder used as the intended matrix for cermet.

Other physical processes that may cause instability during sintering at the temperature above melting point of Cu is potentially swelling caused by lack of wettability in the system with TiB₂ and as the consequence drops of Cu can be released [12].

1.6. Goal of the Present Research

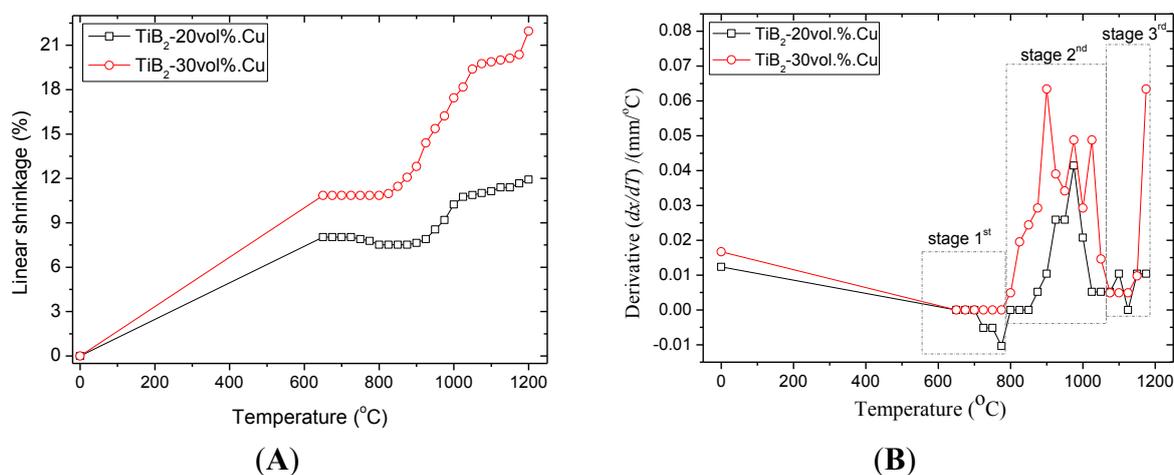
Based on the reference data on vaporizing Cu, it could be assumed that such effect should also be expected during sintering in vacuum, which has not been published so far. Therefore, in order to evaluate quantitatively effects of vaporization, the SPS was applied in this study. Both results of Cu deposition at 1300 °C [27] and most likely solubility of C in Cu at 1500 °C [10] were considered when deciding that the sintering temperature in this study would be limited to 1200 °C. The microstructural investigations and quantitative phase analysis were employed to recognize and identify challenges related to liquid phase sintering of TiB₂-Cu cermets in vacuum. Particular attention was paid to relative density and homogeneity affected by vaporizing Cu. The experimental results are confronted to physical properties of Cu at various temperatures as well as other processes, such as wettability, capillary forces, or grains rearrangement.

2. Results and Discussion

2.1. Effect of Sintering Temperature and Composition on Cu Vaporization

In order to evaluate the effectiveness of liquid phase sintering for TiB₂-Cu cermets by means of SPS and investigate the wettability in this system, which was so far inconsistently reported, sintering process was carried out at two different temperatures: 1100 °C and 1200 °C. Considering that Cu melts at 1083 °C, liquid phase sintering occurred in both cases. Such experiments were performed for powder mixtures with Cu content of 3, 10, 20 and 30 vol. %. In fact, the Cu content affected the densification and homogeneity of cermets significantly. For instance, almost no shrinkage was observed for material sintered with only 3 vol. % of Cu addition, while linear shrinkage exceeded 20% when 30 vol. % of Cu was applied. Based on the graphs for linear shrinkage (Figure 1A), three stages can be distinguished in the sintering process, which are indicated in Figure 1B using derivative function. The first one, up to 800 °C, indicates very low sintering rate, which is manifested by thermal expansion effect exceeding that of shrinkage.

Figure 1. Graphs representing the displacement in Spark Plasma Sintering (SPS) sintering for samples sintered using rapid heating mode: (A) Linear shrinkage with temperature; (B) derivative graph representing changes in linear shrinkage with changing temperature ($dx/dT = f(T)$).

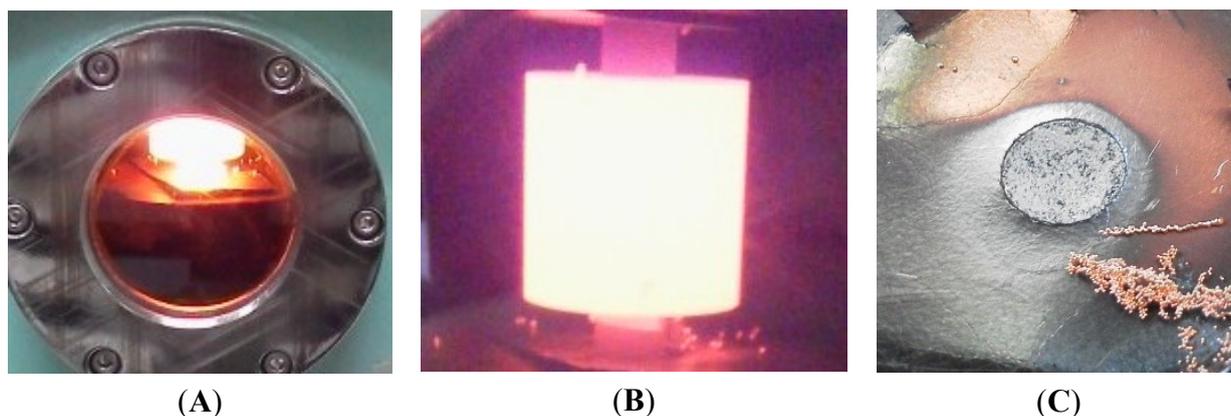


The second stage is characterized by strong multimodal linear shrinkage, which is the consequence of melted Cu and formation of bridge contacts and capillary forces, and finally rapid grains rearrangement. However, this characteristic is caused by more complex processes, including formation of Cu-fume as well as Cu drops at the temperature range of 1000–1080 °C, also related to the fact that high pressure of 30 MPa was applied during sintering. The Cu melt drops released from the graphite die and fume deposited on the protecting graphite foil (Figure 2) resulted in such multimodal displacement behavior.

Finally, the third step corresponds to different sintering mechanisms, such as dissolution, coarsening and grain growth, and retarded shrinkage due to direct contacts between TiB₂ grains. The mechanism of densification corresponds well with theoretical model for liquid phase sintering, where two general stages are expected. The first one is related to TiB₂ grains still sustaining in bridge contact. At the end of this stage relatively rapid rearrangement is completed so direct contacts should exist [24,25].

The second stage is characterized by essentially reduced densification rate since further sintering involves solubility, diffusion, coarsening and grain growth. It means that extended sintering time does not affect densification significantly.

Figure 2. The evidences of Cu evaporated from the die in the Spark Plasma Sintering (SPS) process: (A) drops coming out from the graphite die visible through the window in SPS device; (B) full image of the SPS graphite die with Cu drops on the graphite punches and Cu vaporized on the graphite foil; (C) graphite foil after experiment with Cu deposited from the fume (shown in white dashed lines) and “chains” made of Cu drops (indicated with white arrows).



The effect of reducing Cu content, especially when fine powder was used for sintering, could be expected. Such scenario was discussed by Huppmann [25] and recently mentioned in another study [12], the liquid may move out of the powder compact as a result of mechanical pressure in SPS sintering, thereby creating porosity and a concomitant decrease in density. However, the fact that Cu vaporizes essentially seems to not be considered as a limitation for densification of copper using SPS process, or at least hardly any data on this process are available. Although Zhang *et al.* [14] mentioned that the processes of vaporization and condensation might be a predominant mechanism in the solid phase sintering at 300 °C. Some abnormal behavior manifested by mass loss in thermogravimetric analysis was noticed by Yoon *et al.* [28] for SPS sintering of BaTiO₃ nanoparticles where copper was used as the matrix phase. They interpreted the chemisorbed water or literally incorporated hydroxyl ions in the lattice of BaTiO₃ as the reason of decreasing mass. However, they observed the weight loss in the temperature range of 500–1000 °C, especially for samples with high Cu content while actually volume fraction of BaTiO₃ decreased. Such results most likely indicate strong effect of vaporizing copper, which is consistent with the experiment carried out in this study. Also, the results of linear shrinkage indicated maximum sintering ability in composite with only 15 vol. % of Cu, which corresponded to 92% relative density. The retarded densification observed for increased Cu content, may also indicate deteriorating effect of vaporizing copper.

The effects of simultaneous deterioration in relative density caused by Cu melt moving out from the pellet during liquid phase sintering can be observed in the SEM microstructures (Figures 3 and 4), where essential porosity is visible. Dark grains correspond to TiB₂, while the light matrix consists of Cu. Those materials are characterized by irregular pores distribution, especially when high volume fraction

of Cu was applied. The elongated “channels” most likely are caused not only by poor wettability but also by high vapor pressure of Cu.

Figure 3. SEI of the TiB₂-Cu cermets with various copper content after Spark Plasma Sintering (SPS) at 1100 °C: (A) TiB₂-10 vol. % Cu; (B) TiB₂-20 vol. % Cu, (C) TiB₂-30 vol. % Cu.

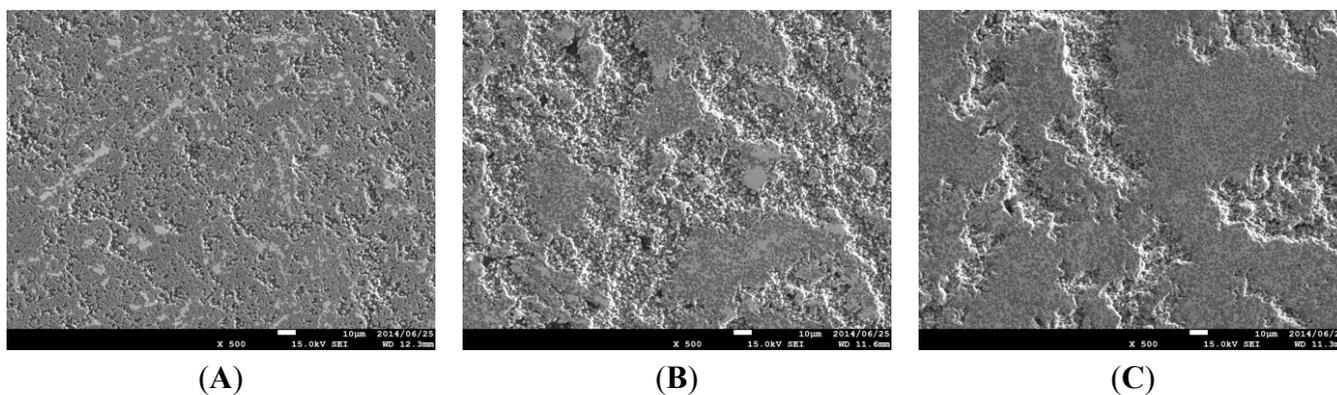
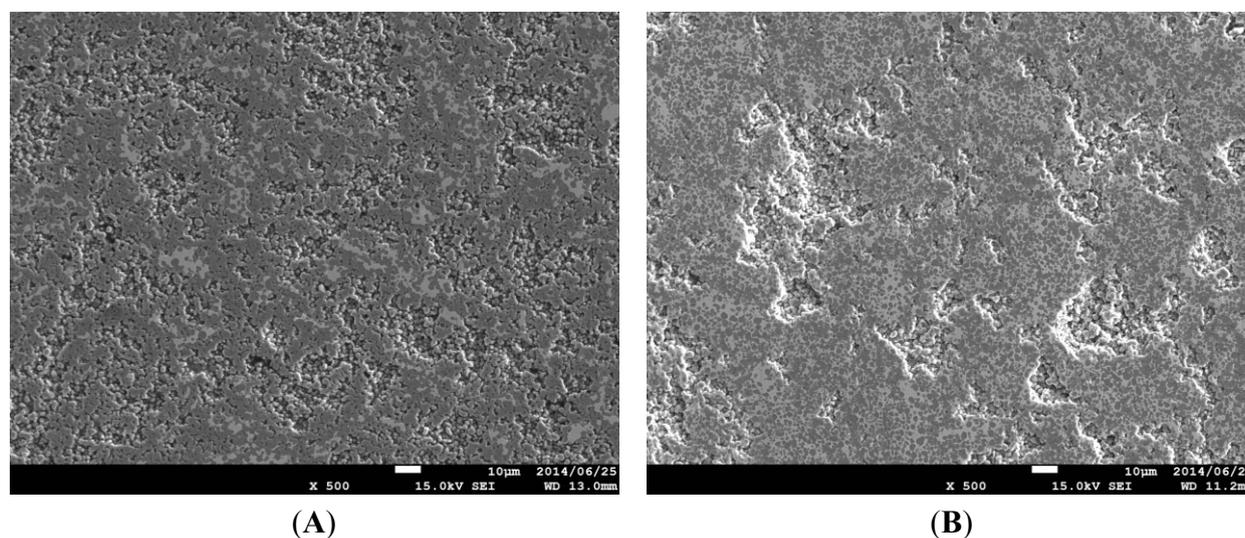


Figure 4. SEI of the TiB₂-Cu cermets with various copper content after Spark Plasma Sintering (SPS) at 1200 °C: (A) TiB₂-10 vol. % Cu; (B) TiB₂-30 vol. % Cu.

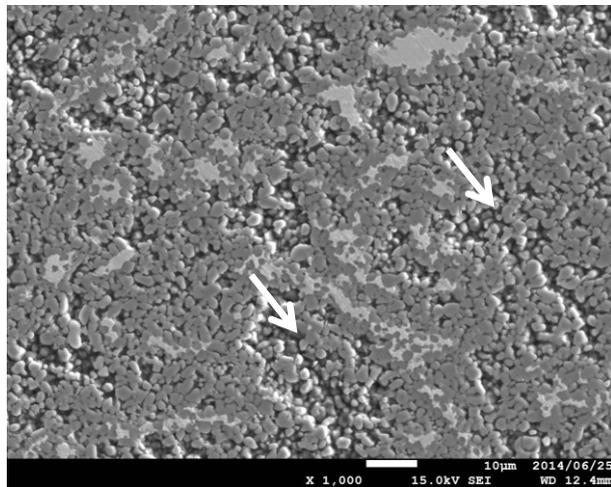
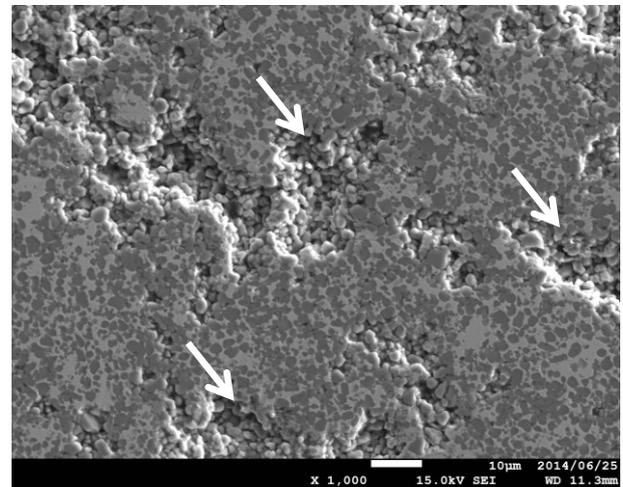
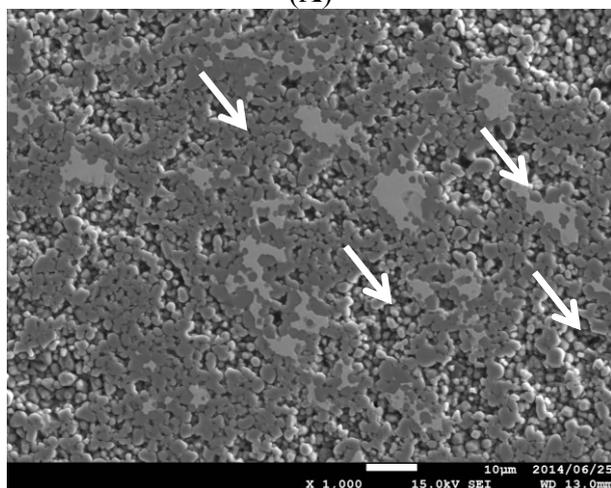
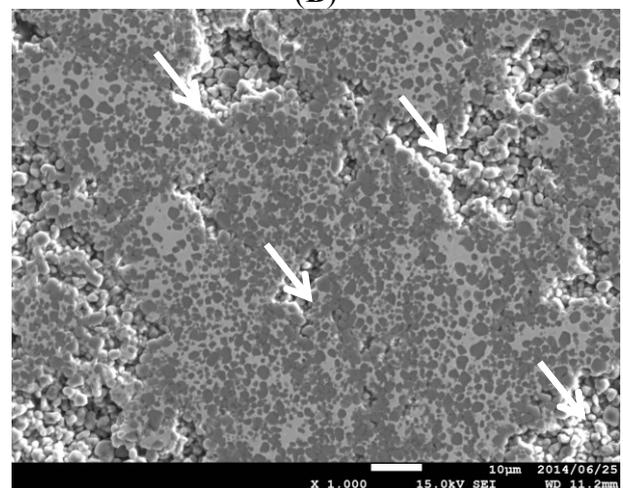
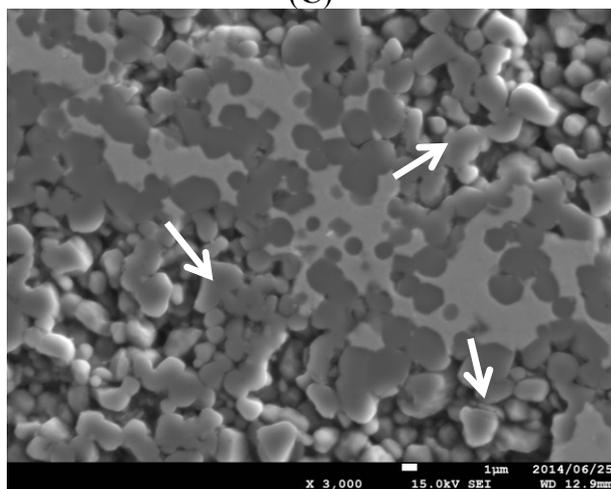
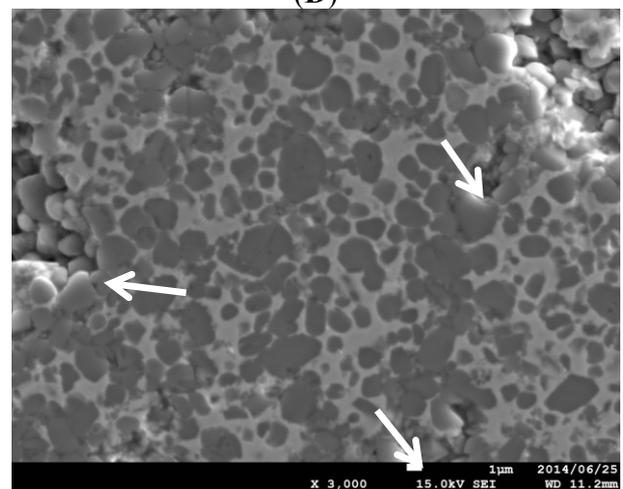


The distribution of Cu in the final microstructure of the cermet is not uniform, especially for material with high TiB₂ content, where several Cu-rich areas could be still observed in cermets sintered at 1100 °C. Such effect indicates limited wettability of TiB₂ by liquid copper and poor effect of capillary forces.

Since viscosity and contact angle are most likely moderated by temperature, further sintering was carried out at 1200 °C. However, the microstructure indicates insignificant improvement in the density and homogeneity in those cermets after SPS at such higher temperature (Figure 4).

The increased sintering temperature caused the average size of Cu-rich areas to decrease in the microstructure. Such effect may indicate both better densifications after grains rearrangement, or just stronger effect of vaporizing Cu. Some areas are entirely infiltrated by liquid Cu, but porosity was not entirely eliminated. The most homogenous microstructure was again observed in composites with the smallest Cu content, as it can be seen especially under high magnification in Figure 5.

Figure 5. The scanning electron image (SEI) of TiB₂-Cu cermets sintered at various temperatures: **(A)** TiB₂-10 vol. % Cu, SPS at 1100 °C; **(B)** TiB₂-30 vol. % Cu, Spark Plasma Sintering (SPS) at 1100 °C; **(C,E)** TiB₂-10 vol. % Cu (different magnification), SPS at 1200 °C; **(D,F)** TiB₂-30 vol. % Cu (different magnification), sintered at 1200 °C. Pores indicated with white arrows.

**(A)****(B)****(C)****(D)****(E)****(F)**

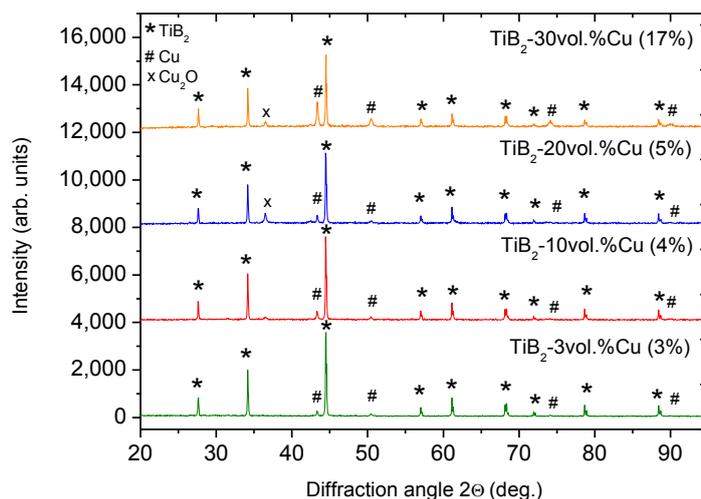
Actually such results are consistent with expectations, the most pronounced rearrangement can be achieved using small amounts of liquid phase because then the detrimental microstructural changes of pore growth are avoided [25]. For small Cu content TiB₂ grains are agglomerated when looking at the microstructure with higher magnification, but at the same time, pores size distribution is narrower. Such effect of agglomeration was enhanced after increasing the sintering temperature.

The results clearly indicated that by increasing the sintering temperatures to 1200 °C wettability could not be improved sufficiently in order to fully densify TiB₂-Cu cermets. Further increase in the sintering temperature or extended sintering time was not considered, due to possible solubility of graphite in the sintered cermet. Such effect of graphite contaminations originated from SPS die has been already discussed. Hypothetical consequences of graphite in copper matrix are at least deteriorated electrical conductivity.

2.2. Effect of Heating Rate in SPS on the Cu evaporation

It has been discussed that essential amount of Cu can be reduced from those cermets as the result of vaporizing Cu, and that effect is clearly confirmed when looking at the X-ray diffraction (XRD) patterns in Figure 6. Experimental volume fractions of Cu (in parenthesis) are much lower than nominal ones.

Figure 6. The X-ray diffraction (XRD) pattern for TiB₂-Cu cermets sintered at 1100 °C for 20 min. The actual Cu contents after Spark Plasma Sintering (SPS) are indicated in parenthesis, after nominal contents.



Since significant amount of Cu evaporated or leaked at higher temperature, rapid heating was applied and the step of isothermal annealing was skipped. The effect of thermal history (heating curve) on the Cu content in the final cermets was investigated by XRD (Figure 7).

The concentration of Cu has changed significantly as an effect of vaporization at high temperature, near the melting point (1050–1100 °C), but also the reduction of copper content (quantitatively indicated in Table 1) occurred as the effect of leaking drops (Figure 4). The volume fraction of Cu was reduced significantly after SPS sintering at 1100 °C. The reduction in the Cu content was the result of two different effects: vaporization of Cu powder at elevated temperature, especially just below the melting

point; and swelling, which affected Cu drops. The Cu drops falling down from the graphite die were observed in the temperature interval from 1030 to 1180 °C (Figure 2).

Figure 7. The X-ray diffraction (XRD) patterns for cermets sintered at 1200 °C and their initial powders mixture: **(A)** TiB₂-20 vol. % Cu cermet; **(B)** TiB₂-30 vol. % Cu cermet; **(C)** graph representing the experimental volume fraction of Cu (determined by Rietveld method) confronted to nominal Cu content.

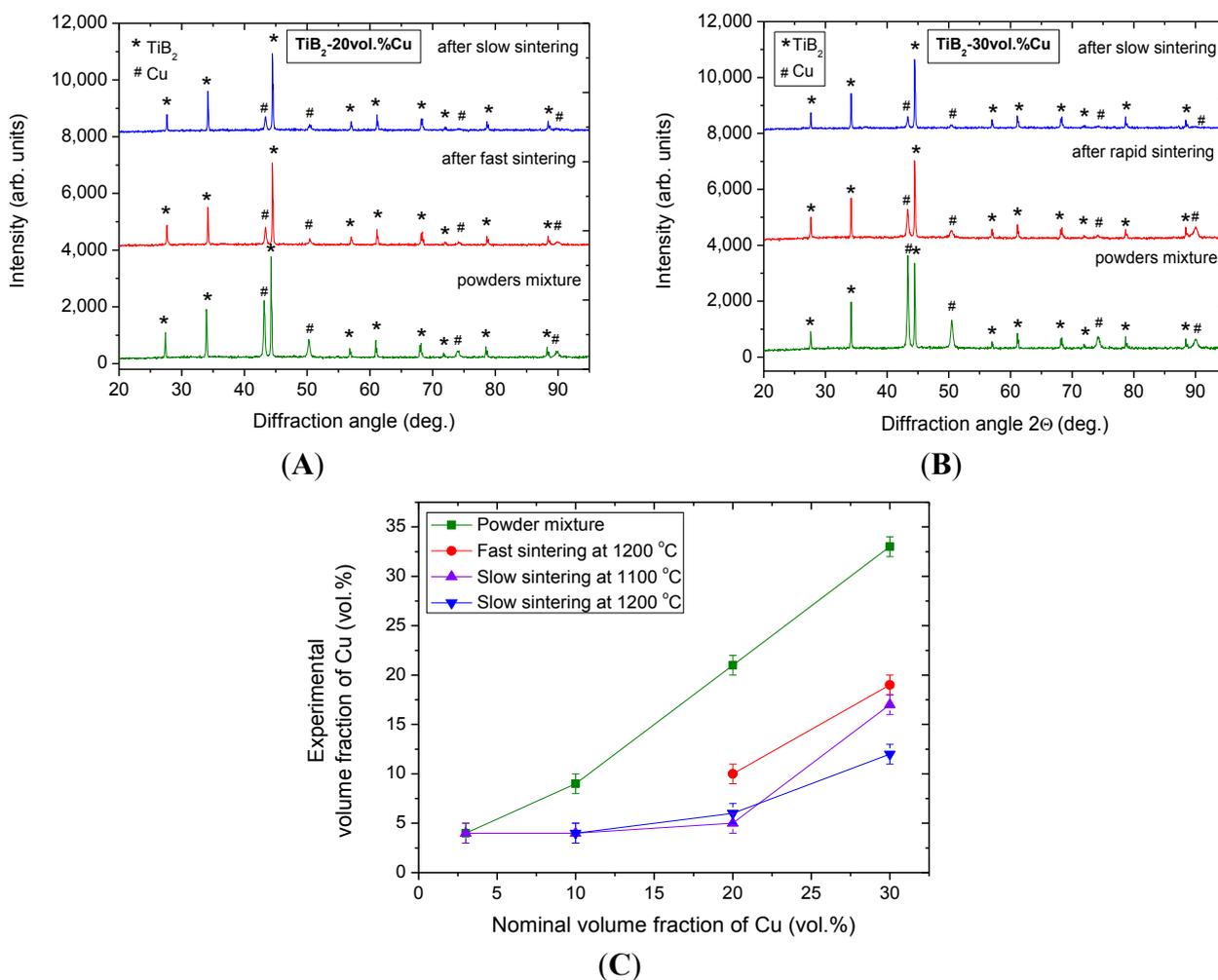
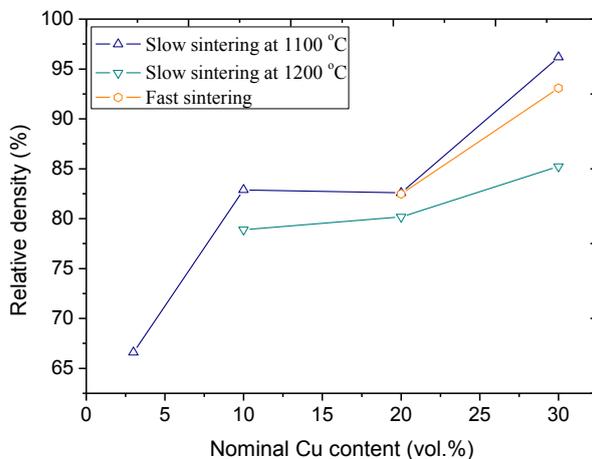


Table 1. Nominal and experimental values of Cu content in TiB₂-Cu cermets after Spark Plasma Sintering (SPS). The numbers indicate volume fraction of Cu, while the value in parenthesis indicates the amount referred to initial content in powder mixture.

Nominal (designed) composition of cermet (vol. % of Cu)	Cu vol. % in powder mixture before SPS	Cu vol. % after low hearing rate		Cu vol. % after rapid sintering
		Sintering at 1100 °C	Sintering at 1200 °C	
TiB ₂ -3 vol. % Cu	4	3 (75.0%)	-	-
TiB ₂ -10 vol. % Cu	9	4 (44.4%)	4 (44.4%)	-
TiB ₂ -20 vol. % Cu	21	5 (23.8%)	6 (28.6%)	10 (47.6%)
TiB ₂ -30 vol. % Cu	33	17 (51.5%)	12 (36.4%)	19 (57.6%)

Based on the results obtained it is evident that Cu addition can improve densification of TiB₂, because relative density of cermets increased along with the volume fraction of Cu, as indicated in Figure 8.

Figure 8. Relative density of TiB₂-Cu cermets calculated based on experimentally determined volume fraction of Cu using Rietveld method.



2.3. Discussion

The results of the present investigations on consolidation of TiB₂-Cu cermets indicate that composites sintered at 1100 °C were characterized by higher relative densities than samples processed at 1200 °C. Such reduced evaporation after applying lower temperature during SPS was manifested especially in sample with maximum investigated Cu content (30 vol. %). Also rapid process with high heating rate reduced the unfavorable effect of Cu evaporation. As the result relative density increased when compared to cermets processed at the same temperature (1200 °C) at lower heating rate. However, the vaporization process can only be impeded, but not avoided entirely by using rapid sintering, which makes controlling the final volume fraction of matrix phase difficult, or even impossible. The Cu content was reduced nearly by half despite applying rapid sintering.

Since liquid Cu occurred in the SPS process, wettability plays significant role in densification. The present study indicated very poor wettability, therefore clear effects of swelling such as Cu drops and fume deposited on graphite elements were observed regardless to composition and sintering temperature. Thus, contact angle between TiB₂ and copper is obviously higher than 90°, even at 1200 °C.

According to results presented by Aizenshtein [21] boron soluble in Cu can essentially improve wettability, which is expected to improve densification in SPS process. Decreased contact angle is most likely caused by an interphase reaction, which was reported previously [17,25]. The increased sintering time did not bring about higher relative density, and even if relatively high relative volume change occurred, it was the result of vaporizing copper. Neither densification could not be improved noticeably despite increased sintering temperature nor were new phases recognized in XRD patterns, which indicated that boron from TiB₂ was not soluble in Cu matrix. Therefore, great thermal and thermodynamic stability of TiB₂ in contact with Cu melt at such temperature range, from 1100 °C to 1200 °C, was confirmed.

According to theoretical models, the rate of macroscopic volume change is higher with increased temperature. It is also expected that shrinkage (or relative volume change) increases with time. However, such theoretical models seemed to be applicable for systems with good wettability, while the present

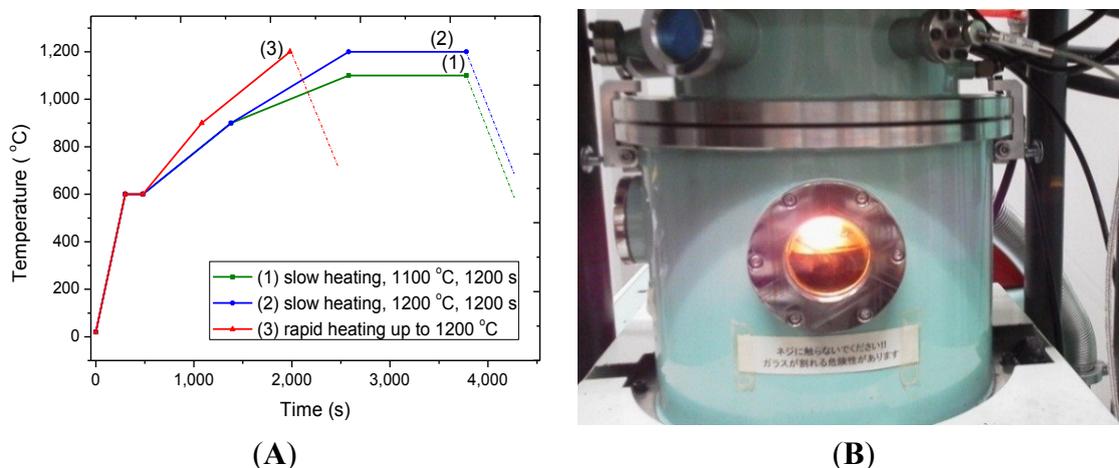
experiments indicated that both the effects of sintering time and sintering temperature are inverted when compared to those theoretical models. Even if the assumption that poor wettability manifested by high contact angle can be partially compensated by increased time of sintering is valid for other systems with limited wettability (the range of contact angle 0° – 45°) [24], it was not confirmed in the present study due to vaporization. The contact angle could hypothetically be reduced by increasing temperature; unfortunately effect of vaporizing Cu is also expected to be strengthened when temperature increases. Indeed, those two processes are competitive.

Taking into consideration that disadvantageous abovementioned effects (lack of wettability and vaporization) the production of fully densified TiB₂-Cu cermet seems to be most likely impossible via liquid phase sintering using SPS techniques in “open device” and vacuum atmosphere.

3. Experimental Section

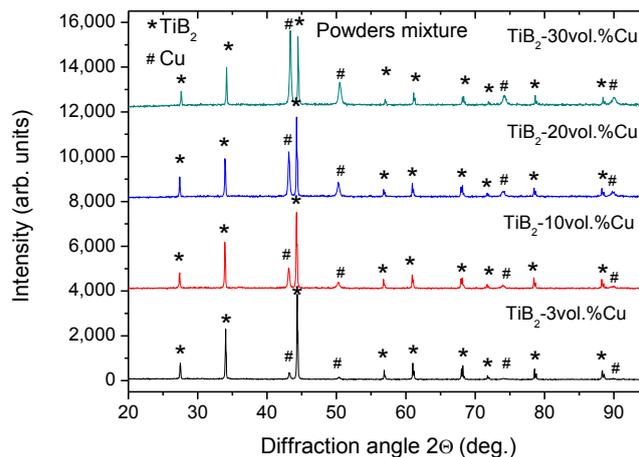
The experiments were performed using the mixtures of commercial powders (TiB₂ 99.7% pure, fraction max 10 μ m, and Cu metal flake 99.9% pure, fraction 1–5 μ m, both supplied by AEE Micronmetals, New York, NY, USA). The volume fraction of Cu was 3, 10, 20 and 30 vol. %, respectively. The powders were homogenized by ball milling technique in 2-propanol, for 3 h. The alcohol was initially evaporated on the hot plate in air, and finally powders were dried in vacuum. Sintering process was carried out in various time-temperature conditions which are presented on the Figure 9A, using “Dr Sinter” SPS device (SPS Syntex Inc., Kanagawa, Japan) (Figure 9B). Powder mixtures were placed in graphite die during the process and the temperature was controlled by pyrometer.

Figure 9. (A) Graph representing the thermal history (heating program) sintering of TiB₂-Cu cermets by Spark Plasma Sintering (SPS); (B) SPS device.



Diamond dispersions were used for polishing of as fabricated materials. Quantitative phase analysis of both powder mixtures before sintering and materials after SPS process were investigated using X-ray diffraction (XRD), combined with Rietveld method [29]. High accuracy of this method used for TiB₂-Cu cermets was validated and confirmed using XRD pattern for the powders mixture before sintering (Figure 10), where Cu content determined by Rietveld method 4%, 9%, 21% and 33%, respectively, corresponded well with nominal composition.

Figure 10. The XRD pattern for powders mixture for powders with the Cu content from 3 to 30 vol. %.



In order to perform the analysis properly, the same reference patterns were applied for semi-quantitative analysis: (01-075-1045 for TiB_2 ; and 01-071-4610 for Cu). High Score Plus, version 3.0d (3.0.4) issue on 01.07.2011, by Panalytical, BV (Almelo, The Netherlands), 2011 was employed as the XRD database. Moreover, the FE-EPMA Jeol JXA-8530F (Tokyo, Japan) scanning electron microscope (SEM) with electron probe microanalyzer (EPMA) was applied to observe the microstructure of samples.

4. Conclusions

The investigations revealed that consolidation of TiB_2 -Cu cermets by means of liquid phase sintering in vacuum using SPS is essentially limited by vaporization of Cu and poor wettability of TiB_2 by Cu melt. All mechanisms involved in the grains rearrangement which affect densification are partially retarded because of those two effects, as the result relative density have been deteriorated with increasing sintering temperature. Even more that 50 vol. % of the initial Cu content was reduced by means of vaporization process in TiB_2 -20 vol. % Cu and TiB_2 -30 vol. % Cu composites sintered at 1200 °C. The effect of vaporizing Cu was quantitatively reduced by applying high heating rate in SPS process; however such effects as essential vaporization below the melting point, Cu droplets released after reaching the melting point and poor wettability still could not be avoided. As the result, neither chemical composition can be controlled, nor porosity entirely eliminated.

There are potentially two effective solutions to fabricate cermet with essentially improved relative density. The first method involves chemical modification of Cu matrix in order to improve wettability in TiB_2 -Cu system. However, such modification may not reduce vaporization sufficiently. Moreover, most modifications will affect the crystallization of additional phases, *i.e.*, intermetallics. The second method to eliminate effects of vaporization and control the chemical composition is by means of fabrication using encapsulated device, as it has been already published [9]. In this case the poor wettability of TiB_2 by Cu and weak effect of capillary forces can be compensated by high pressure working on a well-sealed container, which is able to both enhance infiltration and prevent vaporization of Cu.

Acknowledgments

Author wish to express gratitude to the Main Editor of Metals as well as to MDPI Publishing for a great initiative of the special issue on Advances in Cermets.

Conflicts of Interest

The author declares no conflict of interest.

References

1. Dong, L.; Tao, X.; Hamdi, M.; Zhang, L.; Zhang, X.; Ferreira, A.; Nelson, B.J. Nanotube boiler: Attogram copper evaporation driven by electric current, Joule heating, charge and ionization. *IEEE Trans. Nanotechnol.* **2009**, *8*, 565–568.
2. Eymann, K.; Riedl, T.; Bram, A.; Ruhnnow, M.; Kirchner, A.; Kieback, B. Consolidation of mechanically alloyed nanocrystalline Cu-Nb-ZrO₂ powder by spark plasma sintering. *J. Alloy. Compd.* **2012**, *535*, 62–69.
3. Sharma, A.S.; Mishra, N.; Biswas, K.; Basu, B. Fretting wear study of Cu-10 wt. % TiB₂ and Cu-10 wt. % TiB₂-10 wt. % Pb composites. *Wear* **2013**, *306*, 138–148.
4. Sobhani, M.; Mirhabibi, A.; Arabi, H.; Brydson, R.M.D. Effect of *in situ* formation of TiB₂ particles on age hardening behavior of Cu-1 wt. % Ti-1 wt. % TiB₂. *Mater. Sci. Eng. A* **2013**, *577*, 16–22.
5. Lopez, M.; Corredor, D.; Camurri, C.; Vergara, V.; Jimenez, J. Performance and characterization of dispersion strengthened Cu-TiB₂ composite for electrical use. *Mater. Charact.* **2005**, *55*, 252–262.
6. Zhang, X.; Hong, C.; Han, J.; Zhang, H. Microstructure and mechanical properties of TiB₂/(Cu,Ni) interpenetrating phase composites. *Scr. Mater.* **2006**, *55*, 565–568.
7. Li, G.; Ziemnicka-Sylwester, M. The TiB₂-based Fe-matrix composites fabricated using elemental powders in one step process by means of SHS combined with pseudo-HIP. *Int. J. Refract. Metals Hard Mater.* **2014**, *45*, 141–146.
8. Ziemnicka-Sylwester, M.; Matsuura, K.; Ohno, M. Phase evolution, microstructure and hardness of TiB₂-based Co-containing composite by SHS under pseudo-isostatic pressure. *ISIJ Int.* **2012**, *9*, 1698–1704.
9. Ziemnicka-Sylwester, M. The Cu matrix cermets remarkably strengthened by TiB₂ “*in situ*” synthesized via self-propagating high temperature synthesis. *Mater. Des.* **2014**, *53*, 758–765.
10. Venkateswaran, T.; Basu, B.; Raju, G.B.; Kim, D.Y. Densification and properties of transition metal borides-based cermets via spark plasma sintering. *J. Eur. Ceram. Soc.* **2006**, *26*, 2431–2440.
11. Sigl, L.S.; Schwetz, K.A.; Dworak, U. Continuous turning with TiB₂ cermets: Preliminary cutting tests. *Int. J. Refract. Metals Hard Mater.* **1993**, *12*, 95–99.
12. Biswas, K.; Sharma, A.S.; Basu, B. On the densification mechanisms and properties of Cu-Pb and Cu-Pb-TiB₂ nanocomposites densified using spark plasma sintering. *Scr. Mater.* **2013**, *69*, 122–126.
13. Ritasalo, R.; Cura, M.E.; Liu, X.W.; Soderberg, O.; Ritvonen, T.; Hannula, S.-P. Spark plasma sintering of submicron-sized Cu powder—Influence of processing parameters and powder oxidization on microstructure and mechanical properties. *Mater. Sci. Eng. A* **2010**, *527*, 2733–2737.

14. Zhang, Z.H.; Wang, F.C.; Lee, S.K.; Liu, Y.; Cheng, J.W.; Liang, Y. Microstructure characteristic, mechanical properties and sintering mechanism of nanocrystalline copper obtained by SPS process. *Mater. Sci. Eng. A* **2009**, *523*, 134–138.
15. Brown, C.W. The wettability of TiB₂-based cathodes in low-temperature slurry-electrolyte reduction cells. *Alum. Innov. Part. III JOM* **1998**, *50*, 38–40.
16. Zhang, X.H.; Yan, C.; Yu, Z.Z. *In-situ* combustion synthesis of ultrafine TiB₂ particles reinforced Cu matrix composites. *J. Mater. Sci.* **2004**, *39*, 4683–4685.
17. Nicholas, M.G.; Mortimer, D.A.; Jones, L.M.; Crispin, R.M. Some observations on the wetting and bonding of nitride ceramics. *J. Mater. Sci.* **1990**, *25*, 2679–2689.
18. Mattia, D.; Desmaison-Brut, M.; Tetard, D.; Desmaison, J. Wetting of HIP AlN-TiB₂ ceramic composites by liquid metals and alloys. *J. Eur. Ceram. Soc.* **2005**, *25*, 1797–1803.
19. Ziemnicka-Sylwester, M. Superhard TiB₂-based composites with different matrix fabricated from elemental powders by SHS-p-HIP. *Adv. Sci. Technol.* **2012**, *77*, 146–152.
20. Ahangarkani, M.; Borgi, S.; Abbaszadeh, H.; Rahmani, A.A.; Zangeneh-Madar, K. The effect of additive and sintering mechanism on the microstructural characteristics of W-40Cu composites. *Int. J. Refract. Metals Hard Mater.* **2012**, *32*, 39–44.
21. Aizenshtein, M.; Frage, N.; Froumin, N.; Shipiro-Tsoref, E.; Dariel, M.P. Interface interaction in the (B₄C + TiB₂)/Cu system. *J. Mater. Sci.* **2006**, *41*, 5185–5189.
22. Hwang, K.S.; German, R.M.; Lenel, F.V. Capillary forces between spheres during agglomeration and liquid phase sintering. *Metall. Trans. A* **1987**, *18A*, 11–17.
23. Gessinger, G.H.; Fischmeister, H.F.; Lukas, H.L. A model for second-stage liquid-phase sintering with a partially wetting liquid. *Acta Metall.* **1973**, *21*, 715–724.
24. Xu, K.; Mehrabadi, M.M. A micromechanical model for the initial rearrangement stage of liquid phase sintering. *Mech. Mater.* **1997**, *25*, 137–157.
25. Huppmann, W.J.; Riegger, H. Modeling of rearrangement process in liquid phase sintering. *Acta Metall.* **1975**, *23*, 965–971.
26. Baik, S.; Becher, P.F. Effect of oxygen contamination on densification of TiB₂. *J. Am. Ceram. Soc.* **1987**, *70*, 527–530.
27. Lee, B.S.; Barnes, M.C.; Kim, D.Y.; Hwang, N.M. Spontaneous generation of charged clusters of a few nanometers during thermal evaporation of copper. *J. Cryst. Growth* **2002**, *234*, 599–602.
28. Yoon, S.; Dornseiffer, J.; Xiong, Y.; Gruner, D.; Shen, Z.; Iwaya, S.; Pithan, C.; Waser, R. Synthesis, spark plasma sintering and electrical conduction mechanism in BaTiO₃-Cu composites. *J. Eur. Ceram. Soc.* **2011**, *31*, 773–782.
29. Liu, H.; Kuo, C. Quantitative multiphase determination using the Rietveld method with high accuracy. *Mater. Lett.* **1996**, *26*, 171–175.