W – TiB₂ Composite Material for Electro-Spark Deposition

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Abstract. The W – TiB₂ composite materials were prepared by spark plasma sintering at INM Gliwice, Poland and by solar powder metallurgy at Plataforma Solar de Almeria (PSA), Spain. Composites were prepared by sintering of green compacts of W powder with 60 vol.% of TiB₂ powder. During the spark plasma sintering the sintering temperature was 1800 °C, pressure of 22kN, time of 300 s and heating rate of 1.67 °C/s. In solar furnace the sintering temperature was 1820 °C, pressure less, time 600 s and heating rate of 2.33 °C/s. The resulting composites prepared by spark plasma sintering possess 95 - 97 % of theoretical density. The composites prepared in solar furnace have porosity of 49%. Both composites are brittle and prone to cracking. The following phases were observed by EDS and XRD analyses: After solar sintering only W and TiB₂ phases were observed. After spark plasma sintering WB and TiB₂ phases were observed. The reason is different method of preparation. Finally it was proved experimentally that both composites can be successfully used as electrodes for electro spark deposition of hard wear resistant layers on metallic substrates.

1. Introduction
Titanium diboride (TiB₂) based cermets have recently been studied for their potential applications to cutting tools and wear resistant materials because of their superior thermo - mechanical properties under various conditions [1 -2].

Resistance spot welding [3] is a process in which contacting metal surface points are joined by the heat obtained from resistance to electric current. It is widely used in the automobile manufacturing industry to weld the sheet metal to form a car and is completely automated. A limiting factor in industrial manufacturing using resistance spot welding is the life of the welding electrodes. A short life necessitates frequent electrode dressing or changing, resulting in lower production rates and higher costs. Also, weld quality is more variable towards the end of the life of an electrode, particularly when welding coated steels. Therefore it was proposed to use titanium diboride based coatings prepared by electro spark deposition process [4] on these electrodes containing tungsten insert [3]. However the situation during resistance spot welding is complex and single titanium diboride layers are not fully suitable in this case. Therefore it was propose to use composite electrodes for electro spark deposition. It is expected that tungsten with 60 vol.% of TiB₂ will be proper choice to protect the working surface of resistance spot welding electrodes.
The question is how to prepare desired composition simply and cost effectively. Usually this can be done using powder metallurgy methods. One possibility to prepare dense titanium diboride and tungsten is spark plasma sintering (SPS) [1, 2]. However up to now no experimental work concerning direct SPS of mixtures of tungsten with TiB_2 can be found in the literature.

Recently authors used Solar Powder Metallurgy (SolPM) to study the preparation of fully dense titanium goods using solar furnace via pressure less sintering [5]. It was shown that significant advantage of solar furnace is simple handling and significant shortening of heating/cooling times. Therefore it was proposed to use also this method of preparation of desired composite material. This approach is also brand new from materials science point of view.

Therefore, the aim of the proposed work is to study experimentally a possibility to prepare dense W + 60 vol.% TiB_2 powder compacts using Spark plasma sintering (SPS) and Solar powder metallurgy (SolPM) for electro spark deposition.

2. Experimental
The TiB_2 powder (supplier 3M Technical Ceramics, Germany) of angular shape with grain size < 32μm and d_{50} = 15.5μm (see Fig. 1) was used in experiments as filling phase. Composition of used powder according to supplier is following: Ti > 66 %, B > 29 %, C < 2.0 %, B_2O_3 < 2.5 %, O < 2.5 %, N < 0.8 % and Fe < 0.3 %. Tungsten powder (unknown origin) of granular shape with grain size < 10 μm was used as matrix powder. The powder mixture corresponding to the composition of W + 60 vol. % TiB_2 was dry mixed in Turbula mixture for 30 minutes. The densities of used powders considered prior mixing were: W 19.25 kg.m^{-3}, TiB_2 4.52 kg.m^{-3}.

Figure 1. SEM of TiB_2 powder (left) and the mixture of W + 60 vol. % TiB_2 powders (right).

Figure 2. Used FCT-HP D5/2 SPS machine (left) and schematic diagram of SPS process (right).
Spark plasma sintering was performed directly on green powder mixture using FCT-HP D5/2 SPS machine (FCT Systeme GmbH, Germany) at IMN Gliwice. Into the graphite die of inner diameter of 30 mm 45 g of powder mixture was put prior experiments. Then the die was closed, the inner space was evacuated and the following SPS parameters were used: sintering temperature of 1800 °C, pressure of 22kN, time of 300 s, heating rate of 1.67 °C/s and initial air pressure at process start less than 3 hPa.

After SPS the samples were sandblasted to remove graphite envelope, polished and used directly for metallographic (SEM microscope Zeiss Evo MA10 equipped with EDS spectrometer BrukerXFlash®5010) and XRD observations using XRD7 difractometer (Seifert-FPM, Germany). The density of samples was determined using Archimedes method. It was confirmed that during spark plasma sintering it was possible to achieve 95 - 97 % of theoretical density (10.41 g.cm⁻³). Finally prismatic electrodes □ 5x5 mm with the length of 25 mm were cut from the disks using electric discharge machining for ESD deposition tests.

For Solar powder metallurgy the powder mixture was compacted by uniaxial pressing at 280 MPa, which was optimal pressure for used pressing die. The typical geometry of green compacts before sintering was: diameter of 15.2 mm and height of 9 mm. The compacts were weighted and finally the porosity was calculated using known geometry. The observed porosity prior solar sintering was in the porosity range of 43 - 47%.

The sintering experiments were performed at the horizontal solar furnace SF40 in PSA, Almeria, Spain. SF40 is able to deliver up to 40 kW power at peak concentration ratios exceeding 7000 kW/m². This SF40 system consists of heliostat, shutter, parabolic concentrator and test table [6]. The prepared sample was placed on zirconium plate (400 x 400 x 3 mm). The specimen was placed inside of chamber under the focal spot (see Figure 3). The size of solar spot was approximately 90 mm. Then the chamber was evacuated (approximate value of the vacuum was around 8.10⁻¹ Pa) and argon gas flow was used during experiments.

Experimental samples were sintered using SF40 solar furnace at temperatures between 1770 – 1820 °C for dwell time of 10 minutes under the heating rate of 2.33 °C/s. The temperature was measured using pyrometer (emissivity 0.95) [5]. The final porosity was determined from geometry and the weight of the samples and was in the range of 48 - 50%.

After the experiments the samples were cut and samples for microstructure observations were prepared. Microstructure of samples was observed at PSA’s Materials Lab using Leica DMI 5000 Minverted digital microscope and at IMMS SAS using scanning electron microscope JEOL 7600F, equipped with Schottky thermal-emission cathode (thermal FEG - W-coated ZrO2) as well as energy EDS spectrometer from Oxford Instruments. Finally prismatic electrodes □ 4x4 mm with the length of 8 mm were cut from the disks using electric discharge machining for ESD deposition tests.

![Figure 3. Schematic of SF40 solar furnace: left - vacuum/gas chamber mounted on test table; right - solar spot size during solar test (IR camera picture).](image-url)
3. Results and discussion
The experimental works confirmed that it is possible to prepare electrodes from both composite materials via SPS and SolPM. These electrodes can be successfully used for electro spark deposition of hard wear resistant layers on metallic substrates, see for example Figure 4. While both materials are mechanically stable to be used as electrode for ESD process, significant differences in porosity and composition were observed according to used powder metallurgy densification process.

![Figure 4. ESD deposition of prepared composite material on AW7075 aluminium alloy substrate: left – SPS prepared electrode; right - SolPM prepared electrode. Substrate size of $\phi$ 30 mm x 10 mm.](image)

Primary difference was observed in final porosity of the sample. The composite material prepared by spark plasma sintering possesses 3 – 5 % porosity. On the contrary the composites prepared via solar powder metallurgy in solar furnace have porosity in the range of 43 - 47%. It was observed that both composites are brittle and prone to cracking during cooling process.

The most important difference was observed in microstructure (see Figure 5). The main reasons of microstructure differences are control process parameters such as temperature and applied pressure: Spark plasma sintering at 1800 °C under the pressure of 22kN led to more or less homogeneous microstructure (one dominant phase) with certain amount of pores. It ought to be kept in mind that the outer surface of SPS sample is observed where more voids, pores and defects are concentrated. On the contrary inner microstructure of SolPM prepared composite (sintering temperature 1820 °C and no pressure) is fully porous with two different phases inside of composite material.

![Figure 5. Microstructure of composites prepared by SPS (left) and SolPM (right).](image)

To distinguish the created phases EDS and XRD analyses were performed. Inside the composite prepared at solar furnace only W and TiB$_2$ phases were observed using ESD analyses (Figure 6). Moreover slight expansion of the sample in both axial and radial direction was observed after solar
sintering. This 2 – 4% expansion can be connected with rearranging of the structure due to relaxation of internal stresses created during compacting of powders. The most probably sintering process led to the slight reaction between tungsten and TiB$_2$ powders as solid composite that can be carefully machined was created. Anyway the reaction zone is so small, that it was not possible to detect these phases using XRD analysis. The strength of such material is relatively low and it was quite difficult to avoid cracking of this material during machining of ESD electrodes.

![Microstructure](image1.png)

**Figure 6.** Microstructure of SolPM composite sample and EDS area analyses: Spectrum 1 - TiB$_2$, Spectrum 2 - tungsten.

![XRD Analyses](image2.png)

**Figure 7.** XRD analyses of original green powder mixture and polished SPS composite sample.

Ahn et al. [7] have studied titanium diboride based cermet creation via HIP sintering of green compacts of TiB$_2$–W with compositions between 5 and 40 vol.% of W at a pressure of 200MPa and temperatures above 1750 °C. They have formed cerments with relative density of more than 99%. Analysis of these samples by XRD, EPMA and Auger spectra, showed the presence of TiB$_2$, β-WB and WTiB$_2$. However no metallic tungsten was detected between 5 and 30 vol.% of W. This more or less coincides with the observed phases for both methods of preparation. Moreover it indicates that during solar sintering the real temperature was probably below 1750 °C. According to the literature no reaction
between W and TiB$_2$ occurs up to 1100°C [8]. Strashinskaya [9] observed that in 1 to 5 hour tests the reaction of a powdered mixture of W+TiB$_2$ started at < 1800°C. Compact tungsten reacted with TiB$_2$ powder at 1900°C and with compact TiB$_2$ at 2100°C. All experiments were performed at about 5 x 10$^{-5}$ Torr and tungsten boride phases were formed. According to Gorbacheva et al. [10], titanium borides are stable in contact with W in the temperature range from 1500 to 2000°C. There was neither diffusion of B into W nor adherence of both components to each other; only traces of W$_3$B were detected. Leitnaker et al. [11] observed that tungsten reacted with TiB$_2$ in a mole ratio TiB$_2$ : W = 1 : 1 to form a possibly ternary compound with a lattice close to that of TaB. The formation of WTiB$_2$ as ternary compound was also noted when powder mixtures (grain size < 40 μm) of W and TiB$_2$ (containing - 0.3 wt% C) in the range 0.5 to 100 mol% TiB$_2$ were pressed and sintered at 1800 to 2400°C and pressure of 3.33 Pa. Eutectics appeared on each side of this compound in the quasi-binary system W-TiB$_2$, one at about 12 mol% TiB$_2$, the other at about 88 mol% TiB$_2$ [12].

After spark plasma sintering WB and TiB$_2$ phases were observed in final composite using XRD analysis. It was observed that the main phase is WB phase. WB phase is rhombic with space group of Cmcm # 63 and corresponding space group constants of a = 3.19 Å, b = 8.4 Å, c = 3.07 Å. Further small amount of W$_2$B and TiB$_2$ phases were observed. Due to the rests of graphite envelope on the outer surface of samples also Ti - O,C phase was observed (see Figure 7).

There are following reasons for small reaction of used tungsten and TiB$_2$ powders during SolPM: No applied pressure. Argon protective atmosphere present in solar furnace that is cooling a bit the sample during sintering. The pyrometer readings of the temperature are not precise. For example overestimation of temperature for 6% was observed during solar sintering of Ti [5]. Therefore the real sintering temperature was probably lower for the investigated composite in solar furnace. Moreover, the solar radiation was scarcely 870 W.m$^{-2}$ during October 2017 in PSA, Spain. Therefore at 100% shutter opening it was not possible to achieve higher temperature during sintering of the investigated samples at 40 kW solar furnace. The experiments were done at maximal reachable temperature at given weather conditions. Therefore it is planned to continue these experimental works in solar furnaces with high power flux (SF60, Spain, Odeillo, France).

Summarising, both methods led to the preparation of composite materials that can be successfully used as electrodes for electro spark deposition of hard wear resistant layers on various metallic substrates.

4. Conclusions
The experiments proved that it is possible to prepare W + 60 vol.% TiB$_2$ based composites using Spark plasma sintering (SPS) and Solar powder metallurgy (SolPM) for electro spark deposition electrodes. As no experimental work concerning direct SPS of mixtures of tungsten with TiB$_2$ can be found in the literature this approach is innovative and brand new. Moreover for the first time also Solar Powder Metallurgy was used to prepare W + 60 vol.% TiB$_2$ powder compacts.

Following differences in porosity and composition were observed for both prepared composites according to the used powder metallurgy densification process:

The composite material prepared by spark plasma sintering possesses 3 – 5 % porosity. Composites prepared via solar powder metallurgy have porosity in the range of 43 - 47%.

It was observed that both composites are brittle and prone to cracking during cooling process.

Inside the composite prepared at solar furnace only W and TiB$_2$ phases were observed. Moreover slight expansion (2 – 4%) of the sample in both axial and radial direction was observed. The most probably sintering process led to only slight reaction between tungsten and TiB$_2$ powders. Composite were carefully machined to avoid cracking during preparation of ESD electrodes.

After spark plasma sintering rhombic dominant WB cermet phase was observed inside composite. Further traces of W-B, TiB$_2$ and Ti - O,C phases were also observed in final composite using XRD analysis. The easy machining via electric discharge machining was used to prepare electrodes for ESD deposition.

There are following reasons for small reaction of used tungsten and TiB$_2$ powders during SolPM: No applied pressure, cooling argon protective atmosphere, overestimation of temperature (lower real
temperature inside of material), and limiting power flux at 100% shutter opening at 40 kW solar furnace - the experiments were done at power flux at very good weather conditions. Therefore it is planned to continue these experimental works in solar furnaces with high power flux.

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