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Spark Plasma Sintering – new technology for obtaining tool materials

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Abstract: *Spark Plasma Sintering – new technology for obtaining tool materials*. Cemented carbides are a valued tool material used for tools to process, among others, wood-based materials. They are traditionally obtained using high temperatures and long periods. New electric current activated sintering methods make it possible to obtain sinters with good mechanical properties in a short time and low temperature. This paper presents a comparative analysis of conventional and advanced SPS (Spark Plasma Sintering) technology of obtaining cemented carbides.

Keywords: Sintering; SPS (Spark Plasma Sintering); Tungsten Carbide (WCCo); Composite

CEMENTED CARBIDES

The body of the most commonly used and valued tool material for processing wood-based materials is made of WCCo cemented carbides. WCCo cemented carbides consist of tungsten carbide and cobalt matrix. Due to its properties, cobalt is an excellent matrix material. It has a lower melting point (T_{top}.Co = 1494°C) compared to tungsten carbide (T_{top}.WC = 2785°C), which gives the option to consolidate sinters at lower temperatures and makes it possible to limit the growth of WC grains. Furthermore, Co shows very good wettability (wetting angle is close to 0°).

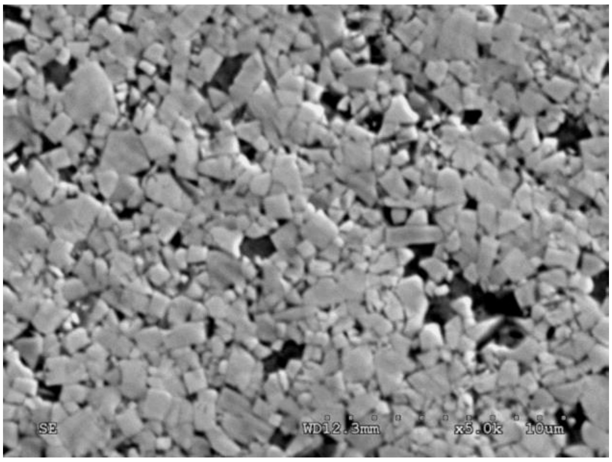

Figure 1. WC6%Co composite microstructure

The properties of WCCo composites change depending on the content of the cobalt phase in the sinter, as well as the grain size. The higher the cobalt content, the higher the bending strength and the lower the hardness (Shin 2000, Ledoux et al. 1992). The hardness and bending strength also decrease with the growth of medium-sized WC grains.

Works (Fang et al. 2017, Lin et al. 2016, Fang 2009) show that carbides of submicron and nanometric grain size have the highest mechanical properties. Grain growth control is the key in the production of the carbides with the finest grains. An effective method of grain growth control is to add a grain growth inhibitor to the powder mixture. The following carbides are used as inhibitors: VC, Cr3C2, TaC, TiC or NbC (Rudy et al.1962, Chen et al. 2017). These carbides dissolve in the liquid phase of cobalt. Mechanisms of blocking the WC grain growth by adding inhibitors are available in numerous published references (Yu et al. 2019, Lay et al. 2002, Lay et al. 2003).

Moreover, the smaller the WC grain size, the longer the tool life. Paper (Sheikh-Ahmad et al. 1999) presents the influence of the WC grain size on the tool wear mechanism. The research covered tools made of WCCo with different average WC grain size (0.4 –1.7 μm) and different content of cobalt (2.5 - 9.5% by weight). Cutting tests were performed on chipboard with a density of 750 kg/m^3. The average cutting speed was approximately 38 m/s. As the WC grain size increased, the hardness of the material decreased and, consequently, tool wear increased. It was proved that the blade wear is caused by the removal of the cobalt binder in the first place as a result of plastic deformation, microabrasion and possibly oxidation. Removal of the cobalt binder also causes the WC grains to crumble and come off the tool material. Therefore, the smaller the size of the WC grains and the lower the cobalt content evenly distributed over the grain edges of the WC grains, the higher the tool wear resistance.

THE CONVENTIONAL METHOD OF PRODUCING CEMENTED CARBIDES

Cemented carbides are obtained by means of powder metallurgy. Conventionally, carbide sintering processes are carried out at high temperatures.

The first step in obtaining cemented carbides is to produce powders. Powder for WCCo carbide sintering processes is usually produced by carburizing pure metal powders or metal oxides. The resulting WC powder is then cleaned and ground. The powder is mixed in ball mills which ensure proper aggregation of the particles. The mixing process is usually made with the addition of agents (e.g. stearin, glycerine, alcohol, gasoline) that reduce friction and facilitate slipping between individual powder particles, therefore facilitating concentration.

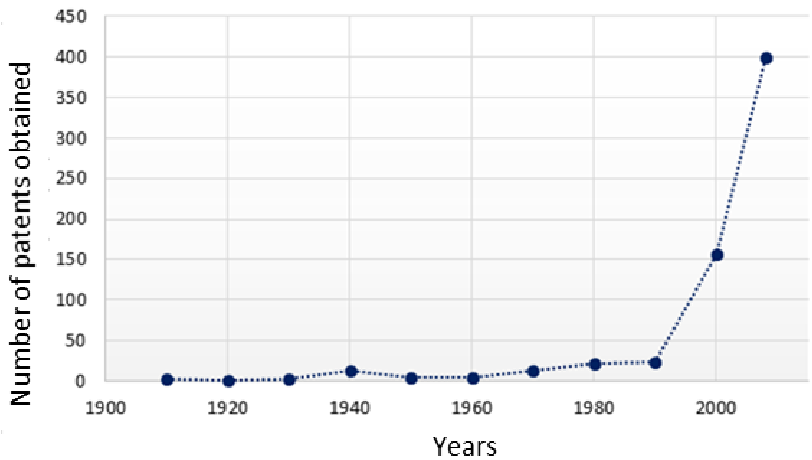

Figure 2. Number of patents obtained (Orru et al. 2009)

The next stage consists of moulding the profiles by cold pressing, which are then pre-sintered. The pre-sintering process is made at a temperature of 1070–1270 K. Then the profiles are finished and undergo final sintering. This sintering stage is made in a reducing atmosphere or vacuum, in ovens with resistance or induction heating. The sintering temperature depends on the cobalt content and is 1620–1730 K. This stage takes several hours. The main disadvantage of the free process of sintering is the necessity to use high temperature and a long time to achieve high-density sinters. These conditions, however, affect the intense growth of grain in the consolidated sinter (Andr´en 2001, Upadhyaya 2001).

Additionally, the cost of tools compared to the price of the processed material is relatively high.

METHODS OF ELECTRIC CURRENT ACTIVATED SINTERING

The body of the first patent for heating a material with the electric current was granted as early as in 1906. However, it was in 1966 that Innoe finally developed the first concept of FAST sintering (Field Assisted Sintering Technology). He filed about 20 patent applications. His work was based on the use of the electric current in the sintering process, for example, low-frequency alternating current (AC) or high-frequency AC or DC. This work led to the development of the current FAST/SPS technology (Shin 2000). The commercialization of the method based on Innoe's patents started in the late 1980 s. Figure 2 shows the number of patents obtained over the years (Orru et al. 2009).

New methods activated by electric current, referred to in the literature as FAST, have been developed in recent years. Such methods are at the heart of interest in the world's largest scientific centres. They are fully applicable for obtaining tool materials such as sintered carbide or high-speed steel.

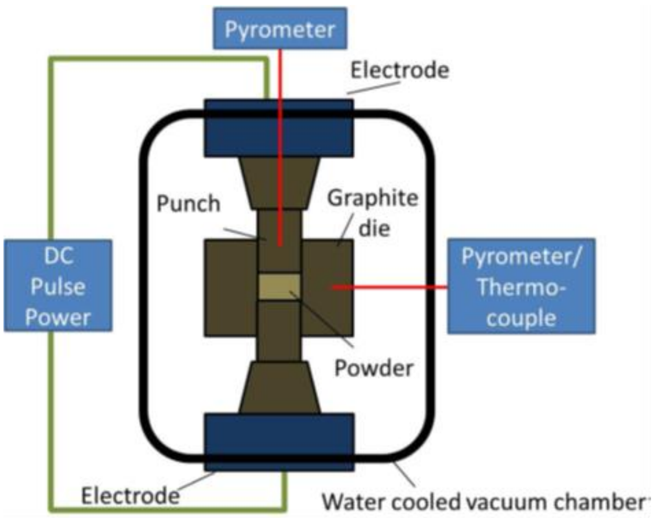

Figure 3. Working schematic of a FAST apparatus (Guillon et al. 2014)

Table 1. Configuration of a typical SPS system (Cavaliere 2019)

Max. temperature attainable lies in the range of 1800–2200°C
Hydraulic press capable of applying a force in the range of 10–400 tons
Heating rate of 5–1000 K/min
Holding time ˜ 2–30 min
Pulsed DC power source providing a current in the range of 3000–40,000A at 1–20 V
Max. power capacity rating of 37–1200 kW
Vacuum in cold oven $5x10^{-2}$ mbar
Process gases – Ar, N_2 (max. 5 bar)
Pulse duration of 1.255 ms and break duration of 0.255

SPS (Spark Plasma Sintering) is the most commonly used of the FAST methods. In the SPS method, the powder is placed in a graphite set (matrix + 2 stamps), which is a kind of heating element when the electric current flows through it. During the sintering process, the whole set is subjected to uniaxial pressure. The powder is heated with Joule heat, which is released during the flow of current pulses through the matrix and the sintered powder. The temperature during the process is measured with a thermocouple placed in the electrode or with a pyrometer (Anselmi-Tamburini et al. 2005, Vanmeensel et al. 2006, McWilliams et al. 2006). The diagram of the method is shown in Figure 3. Typical SPS device parameters are shown in Table 1.

The SPS process takes place with the use of high intensity but low voltage electrical discharges (several Volts). In theory, each newly created pulse should flow in a different way between the powder particles. The effect of the flexible flow of the material results from the pressure applied between the stamps. The combination of this phenomenon with diffusion processes makes it possible to obtain a material with porosity of less than 1% (Herba 2012). The exact sintering mechanism, as well as the role of pulsed current in methods assisted with the electric field, are not fully explained yet. The authors of the paper (Suárez et al. 2013) described the sintering mechanism, dividing it into the following stages:

- activation and cleaning of powder particles surface,
- forming of "necks" between the particles,
- the growth of the "necks" formed,
- the concentration of the material as a result of its plastic deformation.

In the SPS process, thanks to DC pulses flowing through the powder particles, the surface of the powder is cleaned and activated more effectively, compared to conventional sintering methods. Discharges between the sintered powder particles cause local temperature rise, powders' surface melting and, thus, the formation of interconnections between the particles. Therefore, in SPS methods, the thermal energy is released directly in the entire volume of the sintered material. The SPS effect makes these methods highly energy-efficient thanks to a low loss of thermal energy to the environment. In the conventional method, indirect heating occurs through radiation and convection. As a result, there is a significant temperature gradient inside the mould, which translates into heterogeneity in the sintered material (Fig. 4.).

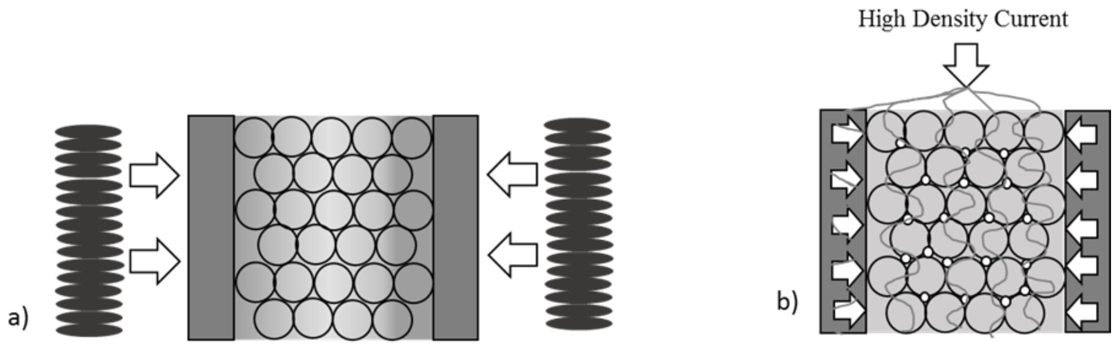

Figure 4. Heating method in a) pressureless b) SPS sintering

The basic difference between conventional sintering and the SPS method is the rate of heating the material. The SPS method makes it possible to heat up at a rate of about 1000°C/min. Zhou and others studied the effect of the heating rate on the properties of aluminium oxide sinters. They have shown that the heating rate in the range of 50–300°C/min has no significant effect on the final sinter density. However, the rate of heating impacts the grain size. With the increase in heating rate, the grain size decreased (Zhou et al. 2003, Munir et al. 2006). In their works (Shen et al. 2002, Vanmeensel et al. 2006), Shen and others demonstrated that the rate of heating up to about 350°C/min did not affect the density of aluminium oxide sinters. An increase in the heating rate to 600°C/min had a negative impact on the density of the sinters received. A clear correlation between the heating rate and grain size was noticed only for lower heating rates (in the range 50–200°C/min). The grain size, as in Zhou's works, decreased with an increase in the heating rate.

As mentioned above, an important parameter when sintering with the SPS technique is the pressing pressure applied. In the study (Rumman at al. 2015), it was found that the hardness of WC–7.5%Co carbides increases with increasing pressing pressure and reaches the maximum value of 1925 HV (18.88 GPa). A reduction in porosity, both in its size and distribution, was also noticed when the pressing pressure was increased.

SUMMARY

The SPS method is one of the most modern techniques of powder material consolidation. This technology has a wide range of applications. It makes it possible to carry out processes at lower temperatures and in a time shorter compared to free sintering. Products sintered in a short time often have better properties than those obtained by traditional methods.

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Streszczenie: *Spark Plasma Sintering – nowa technologia otrzymywania materiałów narzędziowych*. Węgliki spiekane są cenionym materiałem narzędziowym, stosowanym między innymi na narzędzia do obróbki materiałów drewnopochodnych. Tradycyjnie otrzymuje się je z użyciem wysokich temperatur oraz długich czasów. Nowe metody spiekania aktywowane, prądem elektrycznym, umożliwiają otrzymanie spieków, o dobrych właściwościach mechanicznych, w krótkim czasie i niskiej temperaturze. W pracy przedstawiono analizę porównawczą konwencjonalnej oraz zaawansowanej technologii SPS (Spark Plasma Sintering) otrzymywania węglików spiekanych.

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