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Influence of compaction and degassing on the properties of submicron WCCo produced by the PPS method

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Abstract: *Influence of compaction and degassing on the properties of submicron WCCo produced by the PPS method*. The present study is concerned with the effect of the parameters of the degassing operation (temperature, load and heating rate) conducted at the initial stage of the Pulse Plasma Sintering (PPS) process and the sintering temperature at the final stage of the process, on the properties and microstructure of WCCo with a 6wt% cobalt content sintered by this method. The results of the study have shown that when the heating rate is too high, the material obtained is porous. In most experiments, the sintering temperature of 1050°C appeared to be too low to obtain WCCo composites with density close to the theoretical value (GT). Sintering at the temperature increased to 1070°C yielded sinters with density above 99%GT, with hardness of about 1900 HV30 and fracture toughness K_{IC}=9.3 $MNm^{-3/2}$.

Keywords: Sintering; PPS (Pulse Plasma Sintering); Tungsten Carbide (WCCo); Composite

INTRODUCTION

Although the composites of tungsten carbide with cobalt have long been known, they are still the most commonly used tool material, and more than a half of cutting tools at present are made of it [1]. Sintered carbides achieved this great success in the tool industry thanks to their properties, such as high hardness, very good frictional wear resistance, good thermal and electric conductivities, and high stability at elevated temperatures.

Traditionally, tungsten carbide has been sintered freely at a temperature between 1400 and 1500ºC, depending on the cobalt content. The total duration of the sintering process, apart from the time taken by the necessary disintegration and mixing operations, amounts to a dozen or so hours [2].

The last two decades have seen a significant development of the sintering methods that use an electric field to activate the process. This permits an important reduction of the sintering time to less than 20 min (even several minutes). In the literature, these methods are known as EDC (Electric Discharge Compaction). Just as in conventional hot isostatic pressing (HIP), the sintering process is conducted under a uniaxial load, but obviates the drawbacks of HIP which requires a high temperature, a long process time, and in which the efficiency of heating the powder being consolidated is low. The electric-field activated processes differ from HIP in the way in which the heat energy is transmitted to the powder to be consolidated. PPS (Pulse Plasma Sintering) is a modern method belonging to the group of the EDC methods, that permits the sintering process to be conducted at a lower temperature and in a shorter time (about 10 min) [3,4]. The idea underlying this method consists in using electric pulses to heat the powder that is being pressed. The heating is realized through the Joul's heat being dissipated at the contacts between the individual powder particles. Pulses of electric current are generated by discharging a 300 μF battery of capacitors charged to a voltage of several kV.

MATERIALS

The WC6Co (wt%) composites were produced from mixtures of tungsten carbide (94wt%) powder with an average grain size of 0.4µm and ultra-fine-grained cobalt powder (6wt%). SEM images of these powders in the initial state are shown in Fig. 1. The powders were dry mixed in a Turbula-type mixer using carbide balls with a 1:1 ball-to-powder mass ratio. The mixing time was 5h.

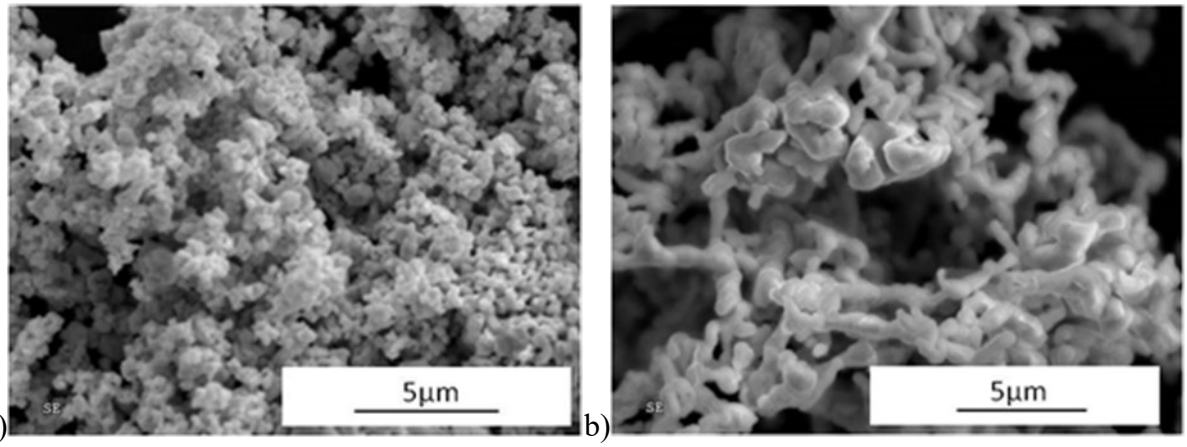

Figure 1. SEM images of the powders (a) WC, (b) Co

The mixture of powders was subjected to initial compaction in a graphite die under a pressure from 5 to 100MPa, using a hand-operated press. The samples prepared thusly were sintered in a PPS apparatus [5]. All the sintering processes were conducted under a reduced pressure of $5x10^{-5}$ mbar in two stages. The first stage included degassing (aimed at removing the absorbed gasses), and the next stage consists of sintering. Degassing was conducted at a temperature (T1) between 600 and 1000°C under a load between 10 and 100MPa with heating at a rate from 700 to 1100°C/min. In the next stage of the process, the sintering temperature (T2) ranged from 1050 to 1100°C. Then, the samples were cooled to room temperature in vacuum of $5x10^{-5}$ mbar at a rate of 160°C/min under a load of 100MPa. The two stages of the process are illustrated schematically in Fig.2.

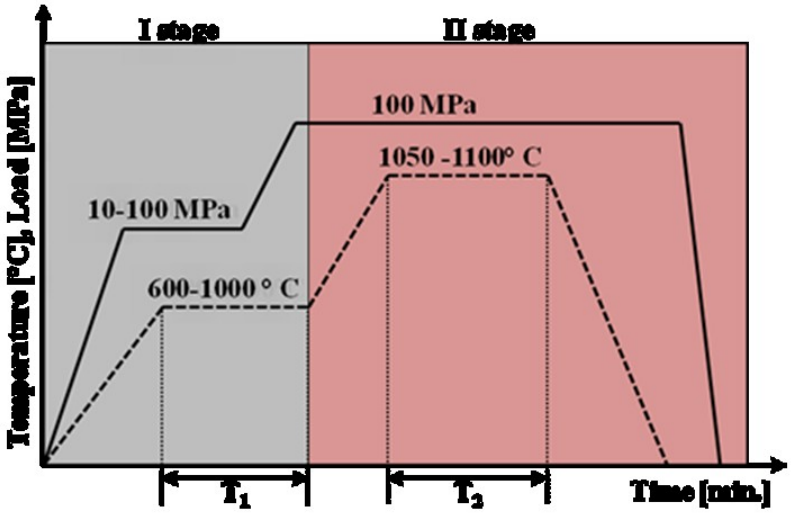

Figure 2. Schematic representation of the course of the sintering process

The microstructure of the sintered samples was observed in a HITACHI S-3500N scanning electron microscope. The images of the microstructures were used for determining the

average WC grain size in the sintered samples [6,7]. Their density was measured by the Archimedes method using a Radwag balance, and their hardness - by the Vickers method in a Matsuzawa VMT-7S hardness meter under a load of 294N (HV30).

RESULTS

Effect of the degassing temperature and the heating rate on the properties of WCCo composites

Figure 3 shows the relative density of the samples sintered at a temperature of 1050°C in dependence on the degassing temperature (600, 900, 1000°C) and the heating rate (700, 1100°C/min). At all the degassing temperatures examined in the present experiments, the samples heated at a rate of 1100°C/min had the relative density below the theoretical value. The highest density was achieved in the samples that were degassed at a temperature of 900°C. The reduction of the heating rate to 700°C/min resulted in a density that slightly exceeded the density of the samples heated with a rate of 1100°C/min, but still much below the theoretical value.

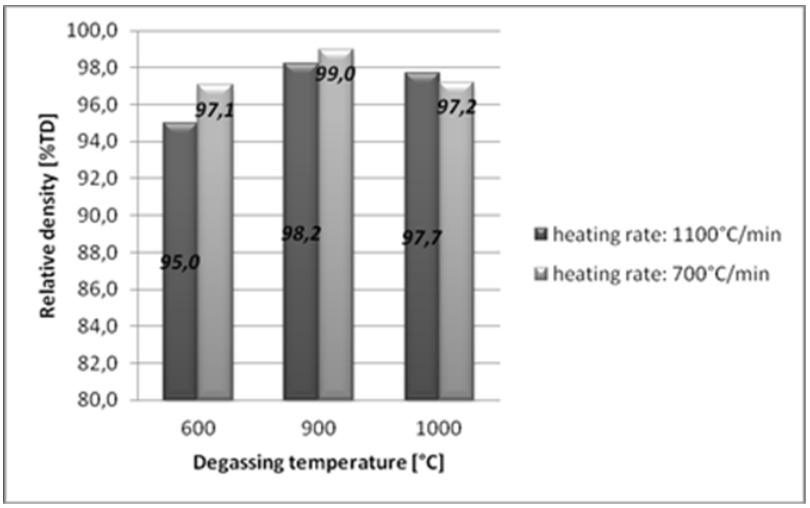

Figure 3. (a) Effect of the degassing temperature and heating rate on the relative density in samples sintered at 1050°C

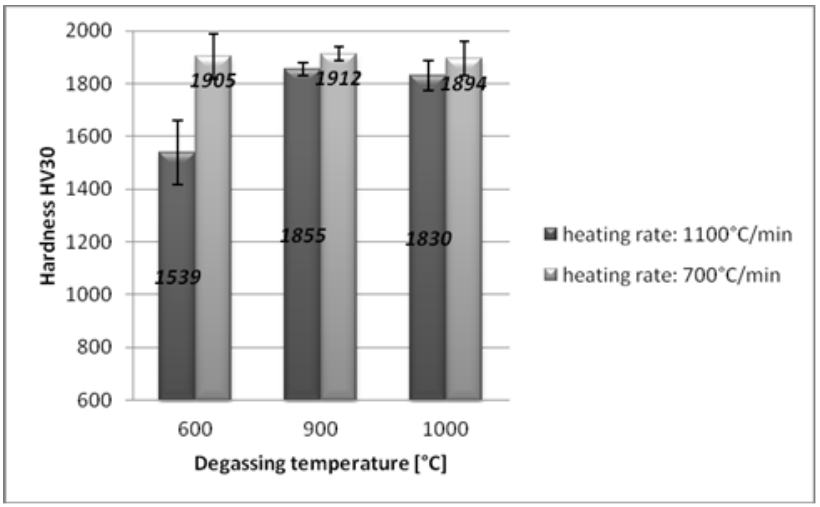

Figure 4. Effect of the degassing temperature and heating rate on hardness in samples sintered at 1050°C

The measured values of hardness show a similar tendency (Fig.4), except in the samples degassed at 900°C with the heating rate of 700°C/min, which had the highest density and the best hardness (above 1900HV30) with the narrowest spread of the measured hardness

values (expressed as the standard deviation), compared to those of the other samples sintered at 1050°C.
Figure 5a shows examples of the microstructure of a fracture of the WCCo composites heated (during the degassing stage) at a rate of 1100°C/min and sintered at a temperature of 1050°C. We can see that the crystalline faces of the WC grains are not fully shaped, with the shapes being similar to those in the starting WC powder (see Fig.1a), and that numerous pores are present in between the grains. Fig.5b shows the microstructure of a fracture of the WCCo composite degassed at a temperature of 900°C with a heating rate of 700°C/min, and sintered at a temperature of 1050°C. The WC grains are well shaped with sharp edges and cobalt distributed uniformly along them forming the so-called paths. No porosity can be observed. The structure is compact and homogeneous on the entire cross-section of the sample, which is confirmed by the hardness distribution.

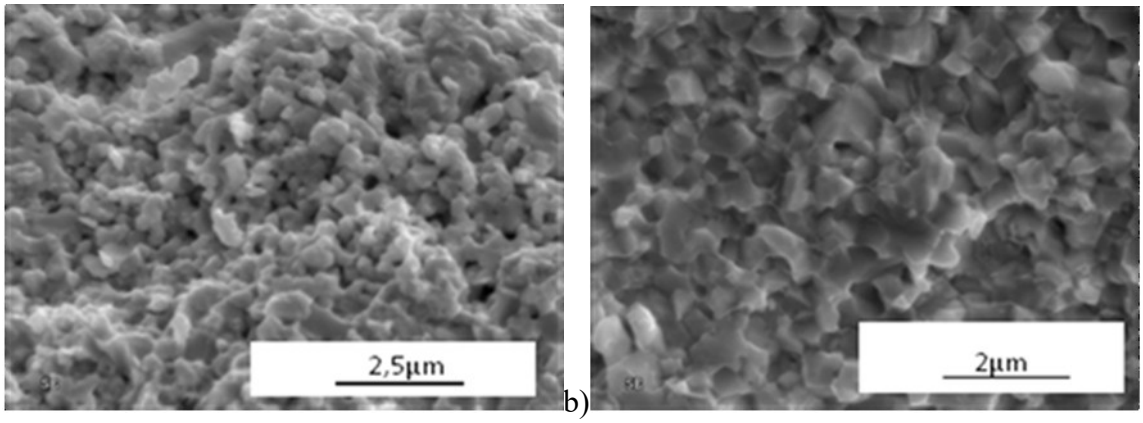

Figure 5. SEM images of a fracture of the WCCo composites: (a) WCCo composite sintered at 1050°C, degassed at 900°C at a heating rate of 1100°C/min, (b) WCCo composite sintered at 1050°C, degassed at 900°C at a heating rate of 700°C/min

As our experiments have shown, heating at a rate of 1100°C/min seems to be too rapid for the material obtained to be dense, compact, and homogeneous. The processes of oxides reduction, evaporation, and condensation taking place during the first stage of the process and resulting in an increase of the inter-particle contact surface, appear to be hampered too much. The material obtained under these conditions is porous and its hardness is low. In the composite degassed at 600 and 1000°C, slightly better density and hardness were obtained with the heating rate decreased to 700°C/min, but it was only the degassing temperature of 900°C and the heating rate of 700°C/min that ensured a dense and homogeneous material.

Effect of the load (at the first stage) and sintering temperature (the second stage) on the properties of WCCo composites

Figure 6 shows how the load applied at the degassing stage affects the density of composites sintered at 1050 and 1070°C. The degassing process was conducted at a temperature of 600°C at the heating rate of 700°C/min. As the load increased, the relative density also slightly increased (from 97.1% to 98.7% of the theoretical value) in the samples sintered at 1050°C, whereas it remained unaffected (above 99% of the theoretical value) in the samples sintered at 1070°C.

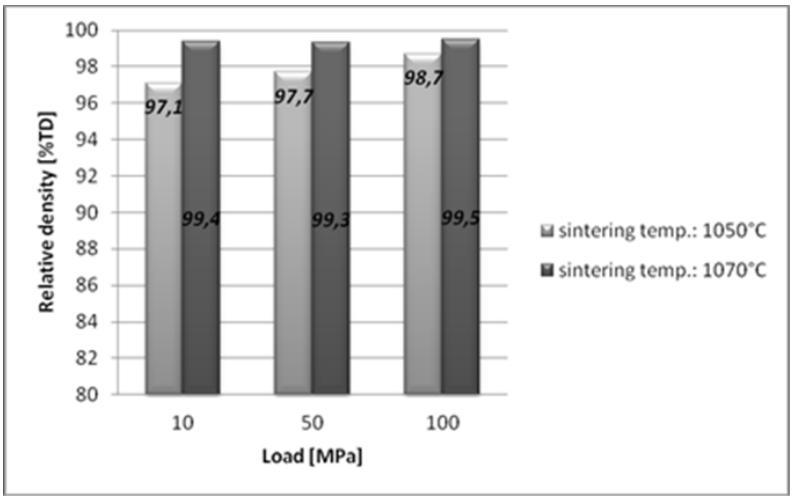

Figure 6. Effect of the sintering parameters (load at the first stage and temperature at the second stage) on the relative density (percent of the theoretical value) of WCCo composites

Figure 7 shows the effect of the load applied during the degassing stage and the temperature at the sintering stage on the hardness of the composites. The lowest hardness (1830HV30) was obtained in the composites sintered at a temperature of 1050°C with the degassing load of 10MPa. Under a greater load (at the same temperature), the hardness slightly increases. All the composites sintered at 1050°C show a wide spread of the measured hardness values, which can be attributed to their poor porosity. The samples sintered at a temperature of 1070°C have a relatively high hardness of 1880HV30 (similar tendency as in the case of density) and the spread of the measured hardness values is narrow. The properties of these samples do not depend on the degassing load.

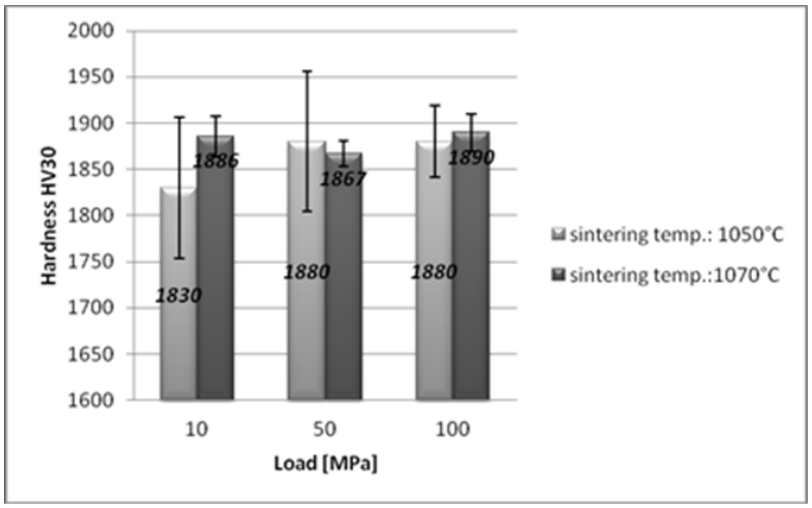

Figure 7. Effect of the sintering parameters (load at the first stage and temperature at the second stage) on the hardness of WCCo composites

Effect of the sintering temperature (II stage of the process) on the properties of WCCo composites

Figure 8 shows how the sintering temperature affects the hardness and density of the composites. The degassing process was conducted at a temperature of 600°C with a heating rate of 700°C/min under a load of 50MPa. The samples sintered at 1050°C had a low density of 97.1% GT. The increase of the sintering temperature to 1070°C results in the density increasing above 99%GT. As to the hardness, it is relatively high (1905HV30) in all the samples sintered at 1050°C, but the spread of its measured values is wide. Only the samples

sintered at 1070°C and 1100°C are characterized by high density and high hardness of about 1800 HV30.

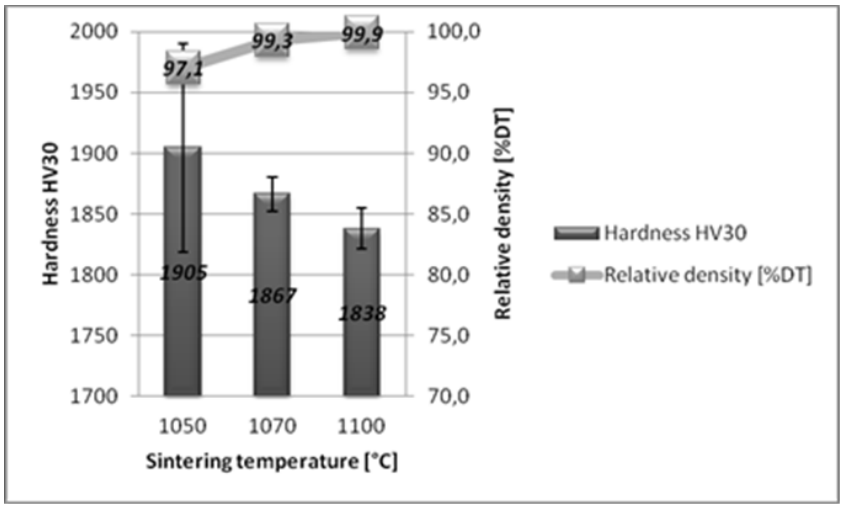

Figure 8. Effect of the sintering parameters (temperature at the 2nd stage of the process) on the hardness and relative density

The slightly lower hardness of the samples sintered at a temperature of 1100°C may be attributed to the presence of small regions (visible on the fracture of Fig.9) in which the grains are larger. The average grain size in these samples is 0.54 μm, whereas that in the samples sintered at 1070°C is 0.44 μm (close to the average grain size in the starting powder which is 0.4 μm).

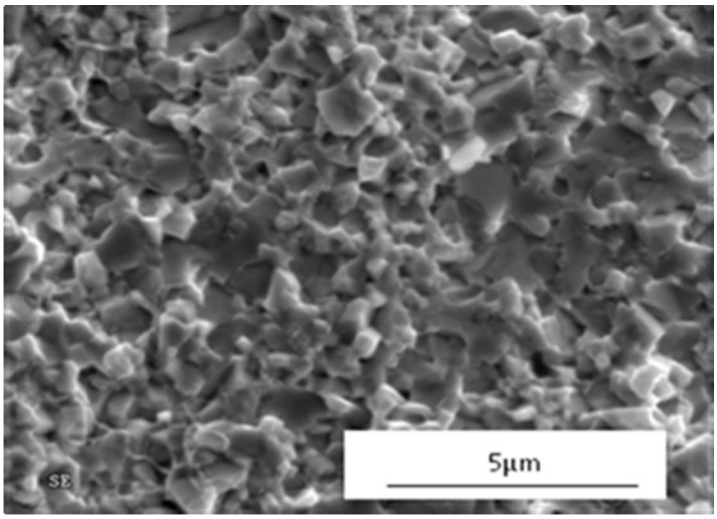

Figure 9. SEM image of a fracture of the WCCo composite sintered at 1100°C, degassed at 600°C under a load of 50MPa

Figure 10 summarizes our results since it shows the effect of the sintering temperature on density (expressed as a percentage of the theoretical value) of the material at various parameters of the two stages of the process. It can be seen that below the sintering temperature of 1070°C, the density decreases. The results obtained for the sample degassed at 900°C at a heating rate of 700°C/min are shown in black in the figure.

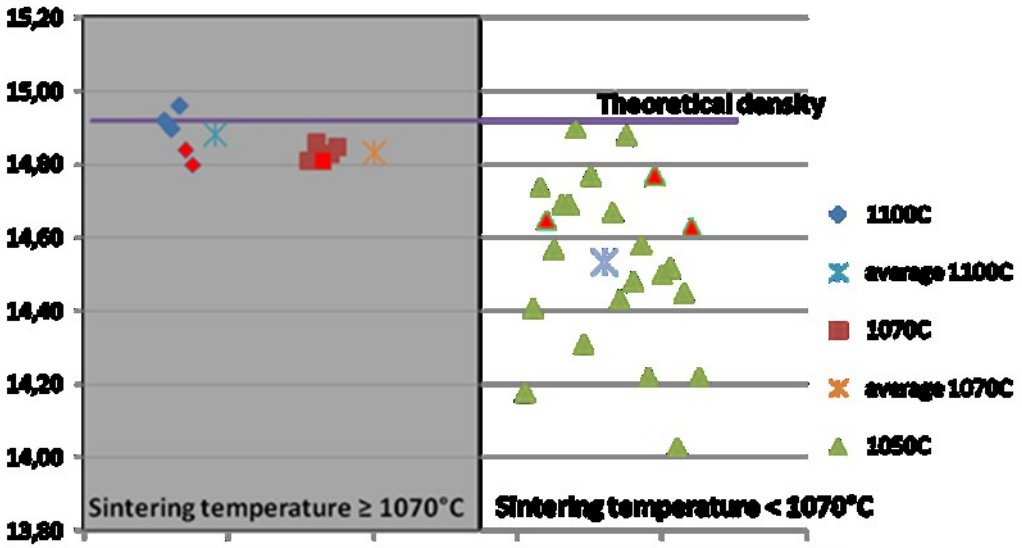

Figure 10. Effect of the sintering temperature on the density of the WCCo composites

CONCLUSIONS

WC6Co composites were produced by the PPS method. The process was conducted in two stages: the material was first degassed under load and then sintered. The effect of the process parameters on the density and hardness of the composites was examined. It appears that, irrespective of the degassing parameters such as load, temperature, and heating rate, the sintering temperature of 1050°C is too low to obtain a compact dense composite except for the samples degassed at 900°C with a heating rate of 700°C/min. Sintering at a temperature of 1070°C permits to produce composites with a density close to the theoretical value.

It also appears that the higher the heating rate, the higher is the porosity of the material obtained and the worse its homogeneity. In the WCCo composites sintered at a temperature of 1070°C, no effect of the load applied during degassing on the properties of the composites was observed.

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Streszczenie: *Wpływ ciśnienia prasowania oraz parametrów etapu odgazowania na właściwości submikronowego WCCo, wytwarzanego metodą PPS*. Węgliki spiekane są cenionym materiałem narzędziowym stosowanym między innymi do obróbki materiałów drewnopochodnych. Tradycyjnie otrzymuje się je z użyciem wysokich temperatur oraz długich czasów. W ostatnich latach nastąpił rozwój nowych metod konsolidacji materiałów proszkowych (określanych, jako EDC - Electric Discharge Compaction), które umożliwiają otrzymanie spieków o dobrych właściwościach mechanicznych w krótkim czasie i niskiej temperaturze. W niniejszej pracy przedstawiono wpływ parametrów etapu odgazowania (temperatury, nacisku oraz szybkości nagrzewania) na właściwości i mikrostrukturę WCCo, o zawartości 6% (wag.) kobaltu, spiekanych metodą PPS. Badania wykazały, iż zbyt duża szybkość nagrzewania prowadzi do otrzymania porowatego materiału. Zastosowanie temperatury spiekania 1070°C pozwoliło uzyskać spieki o gęstości powyżej 99% gęstości teoretycznej oraz o twardości na poziomie 1900 HV30. Średni współczynnik koncentracji naprężeń K_{IC} dla otrzymanych materiałów wynosił 9,3 $MNm^{-3/2}$.

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