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COMPOSITES THEORY AND PRACTICE

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THE EFFECT OF HEATING RATE AND SINTERING TIME ON PROPERTIES OF WC-6Co NANOCRYSTALLINE COMPOSITES PRODUCED BY SPARK PLASMA SINTERING

For the production of composite materials WC-6Co, the spark plasma sintering method was used. As a result of rapid heating and a short sintering time, materials were obtained with a density close to the theoretical value. The resulting sintered materials were measured for density and hardness. The values of the critical stress intensity factor K_{Ic} and modulus of elasticity were set. SEM and AFM observations were carried out. On the basis of X-ray diffractometers analyses, the size of WC and Co crystallites were estimated, whose sizes are less than 50 nm. It was shown that the rate of heating to the sintering temperature significantly affects the sintered microstructure and consequently their mechanical properties. All the sinters are characterized by a K_{Ic} above 11.5 MPa·m$^{1/2}$. The hardest of the obtained materials (1842 HV$_{30}$) was sintered at a heating rate of 600°C/min for 5 min.

Keywords: spark plasma sintering, composite material, WC-Co

WPŁYW SZYBKOŚCI NAGRZEWANIA I CZASU SPIEKANIA NA WŁAŚCIWOŚCI NANOKRYSTALICZNYCH KOMPOZYTÓW WC-6Co WYTWARZANYCH METODĄ ISKROWEGO SPIEKANIA PLAZMOWEGO

Do wytworzenia materiałów kompozytowych WC-6Co zastosowano metodę iskrowego spiekania plazmowego. W wyniku szybkiego nagrzewania i krótkiego czasu spiekania uzyskano materiały o gęstości zbliżonej do teoretycznej. Wytworzone spieki poddano pomiarom gęstości i twardości. Wyznaczono wartość krytycznego współczynnika intensywności naprężeń K_{Ic} oraz modułu sprężystości. Przeprowadzono obserwacje SEM i AFM. Na podstawie dyfraktometrów rentgenowskich oszacowano wielkość krystalitów WC i Co, których wielkość wynosi poniżej 50 nm. Wykazano, iż szybkość nagrzewania do temperatury spiekania wpływa w istotny sposób na mikrostrukturę spieków, a w konsekwencji na ich właściwości mechaniczne. Wszystkie spieki charakteryzują się K_{Ic} powyżej 11,5 MPa·m$^{1/2}$. Najtwardszy z uzyskanych materiałów (1842 HV$_{30}$) spiekany był z szybkością nagrzewania 600°C/min w czasie 5 min.

Słowa kluczowe: iskrowe spiekanie plazmowe, materiał kompozytowy, WC-Co

INTRODUCTION

WC-Co composites due to their favorable combination of soft and plastic Co which combines with very hard and brittle WC, have been used as a material for cutting tools and strained machine building components since the 1930s. These composites are not only characterized by high hardness, which is related to abrasion resistance, but also a favorable fracture toughness and strength. WC-Co composites, as well as other sintered carbides are produced by powder metallurgy methods. The most important methods include conventional sintering in a vacuum at a temperature of 1350 to 1650°C for up to several hours [1-3]. In addition to conventional sintering, in recent years hot pressing (HP) [4], hot isostatic pressing (HIP) [5], microwave sintering [3] and field assisted sintering techniques (FAST) such as spark plasma sintering (SPS) and pulse plasma sintering (PPS) [1, 6] have been used for the production of WC-Co composites. For heating consolidated powder, FAST methods, of which the most popular method is spark plasma sintering, use periodically repeated pulses of DC current that during its flow through the powder causes the secretion of Joule heat. In addition, the pulse nature of the energy supply, lowers the activation energy of the diffusion processes so that the sintering takes place at a lower temperature and in a shorter time than conventional methods. Rapid heating and cooling,

and short sintering time protect the powder grains against excessive grain growth and therefore the SPS method can be successfully used for sintering ultrafine grained or nanostructure powders [7].

The ongoing research on WC-Co composites is intended to increase their hardness while maintaining a favorable fracture toughness (greater than 10 MPa·m$^{1/2}$) [8-10]. For this purpose, the latest manufacturing techniques such as microwave sintering or spark plasma sintering are used. By varying the process parameters, the structure of the sintered materials is modified, shaping the important properties of the sintered carbides such as hardness and brittleness. In the case of the SPS method, the present research focuses on improvement of the mechanical properties of the sintered materials by changing the sintering temperature and sintering time as well as the compaction pressure [8, 11, 12]. Another issue is the heating rate of the sintered materials, which, as has been shown in this paper, is an important contribution to shaping the structure and consequently the mechanical properties.

This paper presents the results of tests of selected properties of WC-6Co composites sintered by the SPS method at 1500°C using various heating rates and sintering times.

EXPERIMENTAL PROCEDURES

For the study a WC-6Co nanocomposite powder was used supplied by Inframat Advanced Materials having a purity of 99.9% which was sintered using an HP D 25-3 (FCT Systeme GmbH) at 1500ºC for 5 and 10 min at a heating rate of 400 and 600°C/min. The compaction pressure was 50 MPa. Sintering took place in vacuum. The sintered materials with dimensions Ø20x6 mm were obtained, which were then tested.

The effective density was measured by the Archimedes method by means of scales PS 750.R2.H (Radwag). Hardness measurements by the Vickers method were carried out using a hardness tester FV700 (Future-Tech) under a load of 294.2 N applied for 7 s. The fracture toughness (K_{Ic}) was determined by measuring the length of the crack by the Palmquist method created during the Vickers hardness measurement, using Shetty's equation (1) [13]:

$$K_{Ic} = 0.15 \cdot \sqrt{\frac{HV30}{\Sigma l}} \tag{1}$$

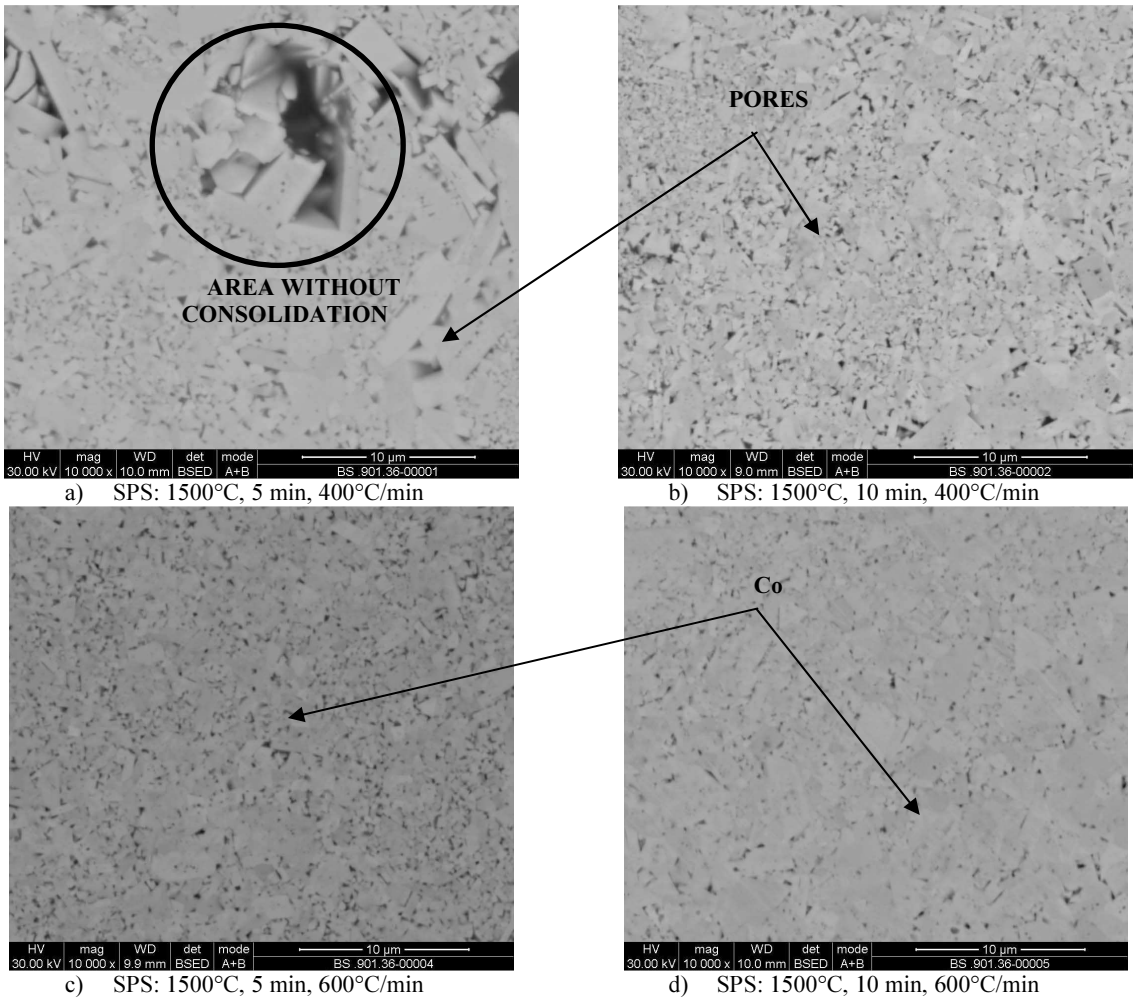
where: $HV30$ - hardness measured under load of 294.2 N, Σl - total length of cracks in accordance with Palmquist method [mm].

The study of the elastic modulus (E_{IT}) was carried out in accordance with EN ISO 14577-1:2002 by means of a Picodentor HM500 (Fischer). A Vickers indenter was used and a load of 300 mN for 5 s. The X-ray structural studies were performed using an Empyrean diffractometer (PANalytical). The tests were performed using $CuK_{\alpha 1}$ radiation with an Ni filter with a stepping working mode. The crystallite size of each phase was estimated by the Scherrer method using Highscore software (PANalytical). Observation of the microstructure was performed on as-received non-etched microsections using a scanning electron microscope (SEM) Inspect S (FEI). A Quesant Q-Scope 250 atomic force microscope (AFM) (Quesant Instrument Corporation) operating in the tapping mode was applied for surface features imaging. Surface scanning was done using a Nanosensors^{TM} Super Sharp Silicon non-contact cantilever (SSS-NCLR), coated with a 30-nm thick aluminum layer and having a resonant frequency of about 140 kHz.

RESULTS AND DISCUSSION

Figure 1 shows the structure of the sintered samples. In the case of the composite sintered for 5 min to a temperature of 1500°C with a heating rate of 400°C/min, there are visible pores the size of several μm, and areas of up to 10 μm in which the material was not fully consolidated. An example of such an unconsolidated area is presented in Figure 1a. In other cases they are fully consolidated. Lack of full consolidation in the first case is directly related to the rate of heating the powder. In fact, increasing the heating rate from 400 to 600°C/min reduces by 50% the time during which the sintered powder is between the initial state and the state in which the sintering takes place at the set temperature. A shorter sintering time translates into a higher energy demand with the objective of temperature growth to 1500°C in a shorter time. Figure 2 shows the change in impulse voltage and current during heating of the samples at 400 and 600°C/min. There is a much higher impulse voltage and current during heating of the powder to the sintering temperature at a higher rate, compared to a slower rate of heating. Spark discharges between the powder particles have a higher voltage and current. In the progressive development of necks, the current density in the neck is also significantly higher in the case of sintering at a higher heating rate. As a result, the diffusion processes run faster, intensifying the sintering process. Thus, the composite sintered at the faster rate of heating at the same sintering time has a better degree of consolidation (Fig. 1a, c). The occurring porosity and areas with incomplete consolidation affect the hardness of the sintered materials. The hardness of the composite, whose microstructure was shown in Figure 1a is 1241 HV_{30} (Table 1) and is considerably smaller than the composites characterized by a solid-like structure (Figure 1b, c, d). The material with the lower hardness is also less brittle, as evidenced by the value of the critical stress intensity factor amounting to 13.93 MPa·m$^{1/2}$. Doubling the sintering time (from 5 to 10 min), regardless of the heating rate, allows us to get full consolidation of the material without visible porosity (Fig. 1b, d). The materials are also characterized by

a much greater hardness of 1724 HV_{30} for the sintered material to be heated to the sintering temperature at 400°C/min and 1815 HV_{30} for 600°C/min. Furthermore, in the case of the composites sintered for 10 min, we observed an increase in hardness of the sintered material with a higher heating rate while the increase is not as large as in the case of the sintered materials for 5 min. The composite sintered for 10 minutes at a heating rate of 600°C/min has a hardness of 1815 HV_{30} which gives an increase in average hardness compared to the sintered composite at the heating rate of 400°C/min of 91 HV_{30}. A favorable resistance to brittle fracture characterizes all the sintered materials - the value of the critical stress intensity factor in all the cases is over 11.5 $MPa \cdot m^{1/2}$, wherein the hardest materials (1842 HV_{30}) have a value of K_{Ic} of 12.39 $MPa \cdot m^{1/2}$. This value is higher by about 2 $MPa \cdot m^{1/2}$, compared to the sintered WC-Co characterized by a similar hardness produced by the SPS method by other authors [6, 8, 11].



a) SPS: 1500°C, 5 min, 400°C/min
b) SPS: 1500°C, 10 min, 400°C/min
c) SPS: 1500°C, 5 min, 600°C/min
d) SPS: 1500°C, 10 min, 600°C/min

Fig. 1. Microstructure of WC-6Co composite sintered using various SPS process parameters, SEM (BSE)

Rys. 1. Mikrostruktura kompozytów WC-6Co spiekanych przy zastosowaniu różnych parametrów procesu SPS, SEM (BSE)

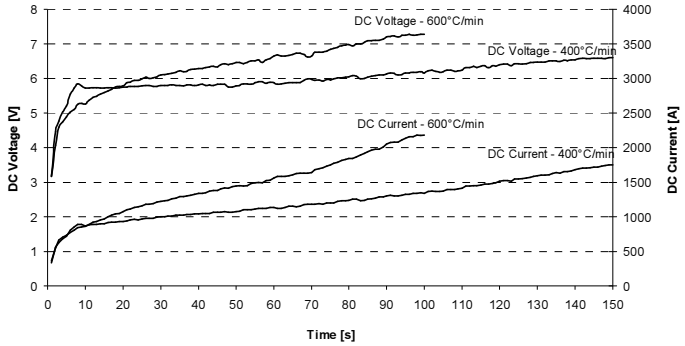


Fig. 2. Change in impulse voltage and current during heating of powder material from temperature of 500 to 1500°C using various heating rates

Rys. 2. Zmiana napięcia i natężenia prądu impulsowego w czasie nagrzewania materiału proszkowego od temperatury 500 do 1500°C przy zastosowaniu różnych szybkości nagrzewania

TABLE 1. **Results of measurements of effective and relative density, hardness, fracture toughness and elastic modulus of WC-6Co composite sintered using various SPS process parameters**

TABELA 1. **Wyniki pomiarów gęstości pozornej i względnej, twardości, odporności na kruche pękanie oraz modułu sprężystości kompozytów WC-6Co spiekanych przy zastosowaniu różnych parametrów procesu SPS**

Heating rate / Sintering time	Effective density [g/cm^3]	Relative density [%]	Hardness [HV30]	Fracture toughness K_{Ic} [MPa·m$^{1/2}$]	Elastic modulus E_{IT} [GPa]
400ºC/min 5 min	14.28 ±0.07	93.79	1241 ±33	13.93 ±1.69	650 ±37
400ºC/min 10 min	14.45 ±0.02	94.90	1724 ±17	11.58 ±1.23	703 ±38
600ºC/min 5 min	14.60 ±0.03	95.89	1842 ±41	12.39 ±0.35	645 ±86
600ºC/min 10 min	14.83 ±0.03	97.40	1815 ±66	11.86 ±0.59	672 ±75

WC-6Co composites produced by the SPS method have a effective density in the range of 14.28 to 14.83 g/cm^3. With an increasing heating rate and sintering time and associated changes in the structure, the density of the sintered materials increases. The material with the highest density (14.83 g/cm^3) determined by the intensification of diffusion phenomena due to high heating rates and long sintering time is the composite sintered for 10 minutes at the heating rate of 600°C/min. The porosity of this material is 2.60%.

The composites obtained by the SPS consolidation method have a relatively high, as for sintered carbides, stiffness - the value of the modulus of elasticity is from 645 to 703 GPa. On the basis of the averaged result of five measurements of the elasticity modulus, it can be concluded that the increase in heating rate of the consolidated powder slightly affects a reduction in the stiffness of the sintered materials, whereas a greater decrease in the E_{IT} (about 31 GPa) was reported for the longer sintering time (10 min). On the other hand, in the case of increasing the sintering time from 5 to 10 min, both for the material heated to the sintering temperature at the rate of 400 and 600°C/min, there appears to be an increase in E_{IT} by 53 GPa for 400°C/min and 27 GPa for 600°C/min.

The results of X-ray phase analysis carried out on polished samples are shown in Figure 3. The resulting composites independent of the SPS process parameters used are characterized by a two-phase structure: WC and Co. All the peaks are characteristic for WC in an angular range 2θ from 30 to 120°. There are also visible peaks with low intensity coming from Co, which are indexed by hkl (111) and (200 indices), similarly as in [14]. The peak derived from Co indexed by the hkl index (220) peak is masked by the WC indexed by the hkl index (200) with a much higher intensity. When using the Scherrer method an estimate of the average WC and Co crystallite size of the powder and sintered materials was made. The results are shown in Table 2. Both the WC and Co crystallites have a size under 50 nm. The smallest size (under 40 nm) is characteristic of crystallites in the composites in which the sintering took place at a heating rate of 600°C/min. When increasing the sintering time from 5 to 10 min, it was observed that the WC crystallite sizes increased while the Co crystallites increased at slower heating and reduced with faster heating of the powder material. By analyzing the effect of heating rate on the growth of the crystallites, at the same time of sintering, it was shown that both WC and Co crystallites are characterized by a smaller size when using the higher heating rate. Furthermore, in all the cases an increase in the average crystallite size as a result of spark plasma sintering was observed.

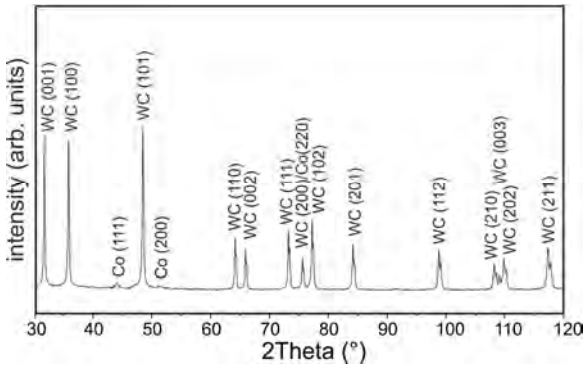


Fig. 3. Exemplary XRD spectrum of WC-6Co composites sintered by SPS

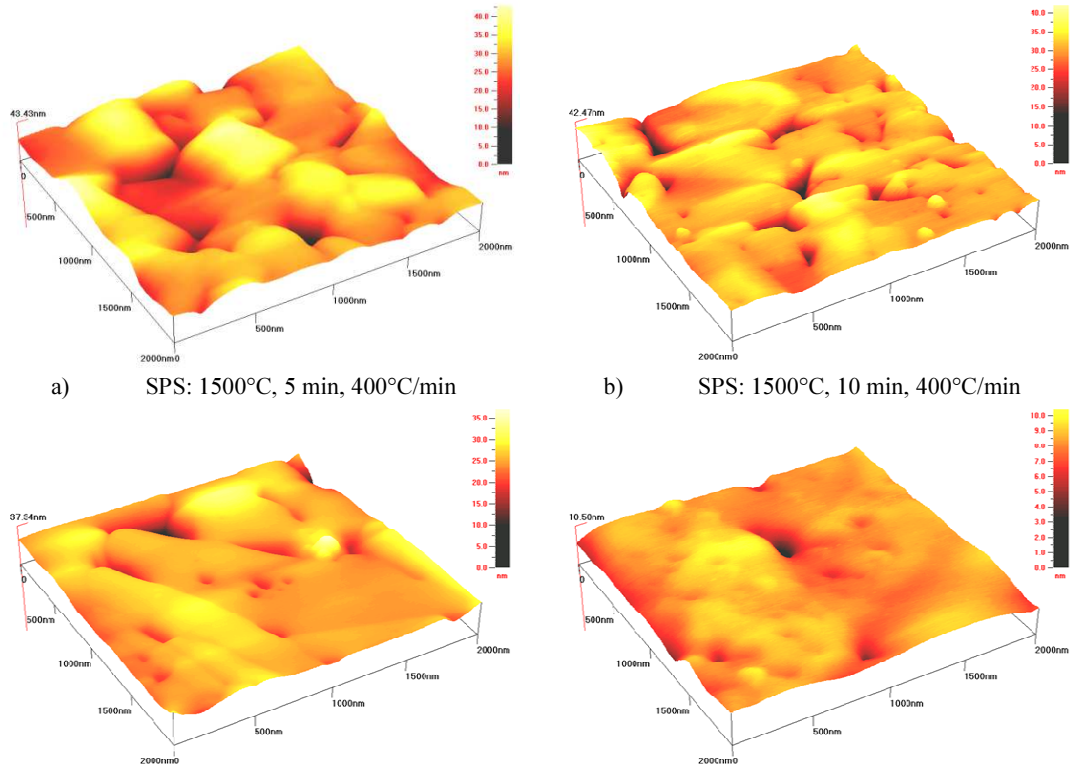
Rys. 3. Przykładowy dyfraktogram kompozytu WC-6Co

TABLE 2. **Size of WC and Co crystallites in composites sintered using various SPS process parameters**

TABELA 2. **Wielkość krystalitów WC i Co w kompozytach spiekanych przy zastosowaniu różnych parametrów procesu SPS**

Heating rate / Sintering time	WC crystallite size [nm]	Co crystallite size [nm]
Powder	29.6 ± 3.9	26.9 ± 3.7
400ºC/min 5 min	41.2 ± 3.7	37.5 ± 3.6
400ºC/min 10 min	45.5 ± 4.4	38.7 ± 4.2
600ºC/min 5 min	31.5 ± 3.5	36.2 ± 3.5
600ºC/min 10 min	39.7 ± 4.1	33.9 ± 3.2

Figure 4 shows the results of the AFM observation. On the basis of the received image, it can be inferred that the WC particles in the case of the composite sintered for 5 min, and heated to the sintering temperature at a rate of 400°C/min, are characterized by a size of approx. 500 nm and a regular multiwall (polyhedral) structure (Fig. 4a). In other cases (Fig. 4b, c, d), the particles have an irregular shape with a length of up to 2 μm and a width of 0.2 to 1 μm.



a) SPS: 1500°C, 5 min, 400°C/min b) SPS: 1500°C, 10 min, 400°C/min

c) SPS: 1500°C, 5 min, 600°C/min d) SPS: 1500°C, 10 min, 600°C/min

Fig. 4. AFM topography image of WC-6Co composites sintered using different SPS process parameters

Rys. 4. Obraz AFM topografii powierzchni kompozytów WC-6Co spiekanych przy zastosowaniu różnych parametrów procesu SPS

The increase in heating rate and sintering time affected not only a change in the shape and size of the particles, but also the sinters surface topography.

CONCLUSIONS

As a result of using the SPS method to consolidate a WC-6Co nanocomposite powder, sintered materials with an effective density of 93.38 to 96.98% of the theoretical density were obtained. The final properties of the composites were formed by changes in the structure of the sintered materials resulting from the use of two variants of heating rates (400 and 600°C/min) and two variants of sintering time (5 and 10 min). The sintering temperature for each time was 1500°C and pressing pressure of 50 MPa. It was proved that both the heating rate and sintering time significantly alter the properties of the materials. Sintering at a higher heating rate enhances the sintering process, because the voltage and current of the spark discharges between the sintered powder particles is much higher compared to slower heating. Therefore the greater the current density in the formed necks. Diffusion processes are activated at a lower temperature and take place more intensively. In the case of an increase in sintering time we also observed improvement in the properties of the tested materials. The best properties were achieved at the highest heating rate to the sintering temperature and the longest sintering time.

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