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Initial stage sintering of binderless tungsten carbide powder under microwave radiation

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Abstract

This work represents an investigation concerning neck growth kinetics during microwave sintering of free-packed spherical shaped binderless tungsten carbide particles. Application of classical sphere-to-sphere approach showed possibility to identify main diffusion mechanisms operating during initial stage of microwave sintering of tungsten carbide powder. An anomalous neck growth in the initial period during microwave sintering was also revealed, which was then followed by neck growth obeying mechanisms of volume and surface diffusion. Numerical simulation of neck growth process revealed anomalous values for diffusion coefficients – 7.16×10^{-13} and 3.41×10^{-8} $m^2\ s^{-1}$ for 950 and 1200 °C respectively. The value of activation energy of neck growth process has been calculated as 69.18 kJ mol^{-1}. That value is significantly lower then any data on activation energy of diffusion processes in W–C system, and may be explained by overheating in the neck zone, or even formation of liquid phase in the neck area.

Keywords: A. Sintering; Microwave heating; Neck growth kinetics; Tungsten carbide; Ceramics

1. Introduction

The use of microwaves to materials processing has been studied in last two decades and now finds application to a wide variety of materials. Initially, microwave heating was successfully applied to sintering mainly of oxide and some non-oxide ceramics [1,2], but latest developments expanded microwave processing to sintering of metal powders and metal-like compounds to theoretical density [3]. Further research of microwave processing revealed a remarkable energy and time saving, which are usually supported by enhancement in mechanical properties with respect to conventionally treated ones [4,5], mainly due to more uniform and volumetric nature of microwave heating.

It is well recognized that microwave heating is accompanied with ''non-thermal effects'', caused by alternating microwave electromagnetic field, and often attributed to enhance sintering process by improving densification and limiting the grain growth, etc. [6]. Some researchers [7] suggest that it is due to the fact that the microwave electromagnetic field promotes atomic diffusion. Other reports [8] suggest that pre-exponential coefficients are different for enhancing diffusion process, rather than diffusion coefficient as it is not dependent on the frequency. Works of Freeman and co-workers [9], indicate that the microwave field has direct influence on ionic conductivity, as an additional driving force, as electric field promotes transfer of charged vacancies on grain surface, hence causes easily plastic deformation of grains, thus promoting the sintering.

While origin of enhancement during sintering process under microwave treatment is still debatable, the model experiments that are focused on sintering kinetics rather than on diffusion coefficients should be carried out. Some of them were conducted on ceramics and included dilatation [10] and grain growth kinetics [11]. Some theoretical work was made by using

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classic flat-ball model for initial stage of conventional sintering and comparing it with data for microwave sintering [12]. Application of sphere-to-sphere model during microwave sintering of copper powder [13] was made, revealing some anomalous neck growth rate during microwave sintering process. These works indicate that experiments for initial stage of microwave sintering could be a missing link to explain the nature of entire microwave sintering process.

Therefore study of neck growth kinetics by exploiting classical sphere-to-sphere contact model [14] was proposed as model experiment for studying initial stage sintering of binderless spherical shaped tungsten carbide powder. Later it was recently successfully consolidated without any binders via Spark-Plasma Sintering method (SPS) [15,16], while WC-Co hardmetals were previously rapidly consolidated by means of microwave sintering [3].

2. Materials and methods

In this study superhard fused spherical tungsten carbide powder was used (Rilit^{TM}, manufactured by Paton Electric Welding Institute, Kyiv, Ukraine). Particle size distribution (SEM, MasterSizer 2000, Malvern) and phase/chemical analysis by XRD/EDX techniques were used to characterize initial powder.

A series of classical neck growth kinetics experiments was conducted using sphere-to-sphere approach [13], in order to investigate diffusion mechanism that controls initial stage of microwave sintering. A monolayer of free packed tungsten carbide particles was placed on microwave transparent mullite substrate, which was then placed inside the insulation package. Sintering experiments were carried out using a 6 kW, 2.45 GHz multimode microwave cavity. No additional susceptors were used in the experimental setup, so that the heating was pure microwave heating, detailed information of the experimental set-up is presented elsewhere [13]. Inert atmosphere was maintained during sintering process by first creating a vacuum of 8–10 Torr inside the furnace by back filling ultra high purity (UHP) nitrogen. Throughout the sintering, nitrogen gas flow was maintained at 2 L min^{-1}.

To avoid additional distortions in electromagnetic field distribution and loss of accuracy in temperature measurements [17], the temperature was monitored using infrared pyrometer Raytek MA2SC (working temperature range 350–2000 °C) and recorded in situ by interfacing with a computer. After the sintering temperature was reached, the isothermal holding was applied. After sintering, the microwave power was switched off and the samples were allowed to furnace cool. The batch of sintered spheres was examined by SEM (Hitachi S-3500N) to investigate neck's size and structure. Neck size was measured for both fractured necks and particles in contact. To ensure validity of measured data, the number of necks measured for every point exceeded 15, an average data on neck size was used as x, $x = (1/m)\sum_{i=1}^{m} x_i$, where x – neck size in μm, and m – number of measurements of neck at given sintering conditions, $m \geq 15$, an average particle size was also collected in similar manner. Groups of spheres in contact were also checked for decrease in the center–center distance, the relative centers' approach was measured (dL/L_0) [18]; the mean value of more then 10 measurements was used in the discussion below.

3. Results and discussion

3.1. Heating of WC powder

Microwave processing of WC powder is usually [3] associated with quick heating, thus no susceptors or binders that absorb microwave energy were used. Pyrometer starts recording the temperature from 350 °C, it took about 3 min to heat up WC to the temperature of recording. Then heating to a set temperature was carried in the multimode regime with constant power of 1.75 kW, to ensure a constant heating rate during all experiments. The microwave power level was reduced to maintain a constant sintering temperature for a fixed holding period (Fig. 1). The reflected microwave power was also monitored, therefore during sintering experiments it was constantly close to zero point. Sintering temperatures were set at 900, 950, 1200 and 1400 °C, and a soaking time from 0 to 120 min was employed.

3.2. Characterisation

The particle size distribution of tungsten carbide powder revealed that mean particle size is 127.7 ± 5.2 μm with a monomodal PSD curve (Fig. 2). SEM measurement of particle size gave mean value of 120.2 ± 7.4 μm and particle shape to be spherical (Fig. 3). EDX (Fig. 3) confirmed that W and C as the major elements present, with oxygen about 1.09 wt%. Oxygen is more likely to be present as free oxygen adsorbed at the particles surface because no oxide phases have been found using XRD. XRD pattern for initial powder shows WC as major phase and some traces of W_2C phase (Fig. 4), caused by powder production method.

Further analysis of XRD patterns reveals that with increase in temperatures to 1200 and 1400 °C, WC remains as a major phase with some presence of W_2C, which was present in the

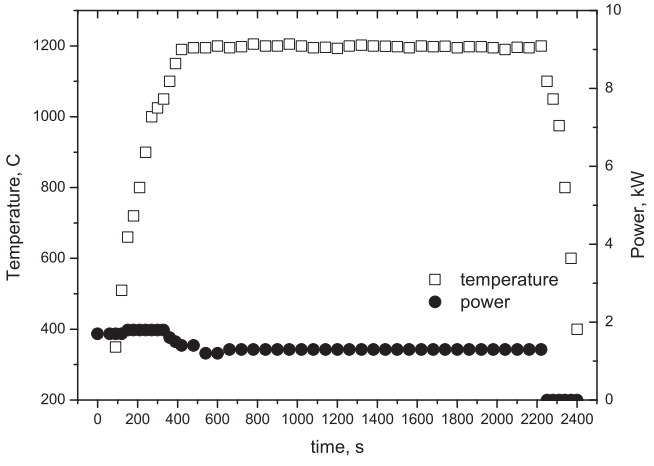


Fig. 1. Time–temperature profile during microwave sintering of WC powder at 1200 °C, 30 min of soaking.

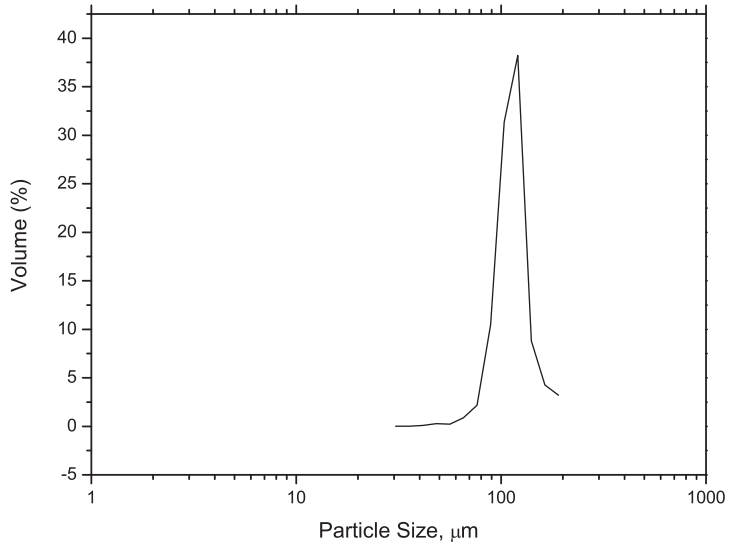
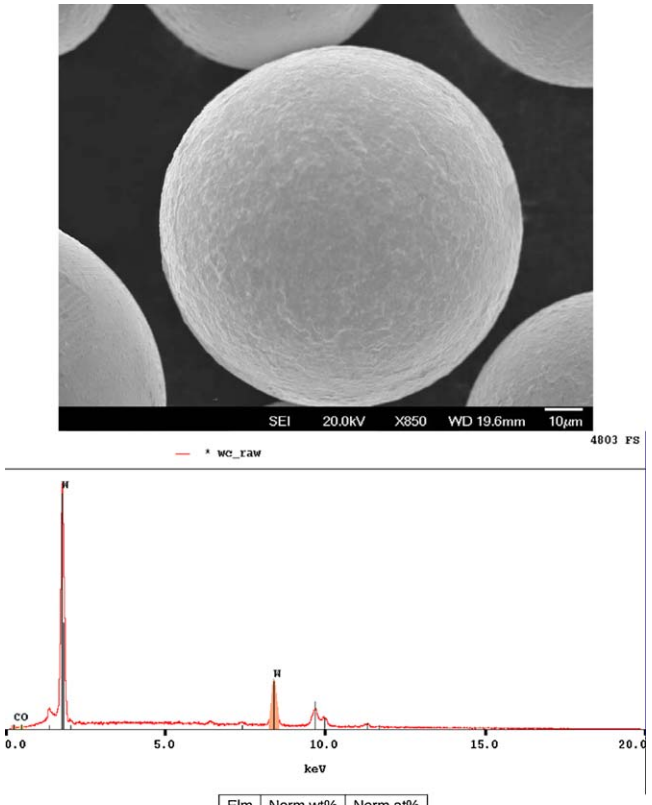


Fig. 2. Particle size distribution for spherical shaped tungsten carbide powder used in present study.

initial powder itself. Formation of carbon free tungsten might be the consequence of purification of surface area from oxides of tungsten or adsorbed oxygen during rapid heating to the sintering temperature, and possible reactions of free-carbon (0.1 wt% according to manufacturer) with oxidized zones. The huge difference in diffusion activity between W in WC and C in WC [19] might be also a reason of formation of carbon free surface of tungsten particles.



Elm	Norm wt%	Norm at%
C	3.56	38.02
W	95.35	61.86
O	1.09	0.12

Fig. 3. EDX/EDS analysis of initial powder.

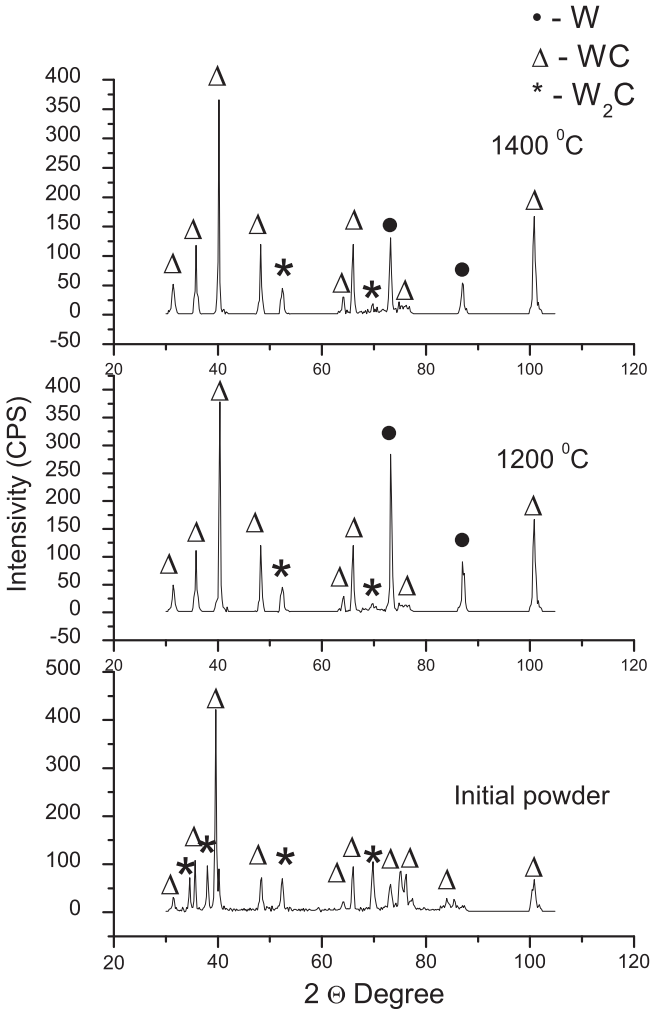


Fig. 4. XRD patterns of sintered WC powders at 1200 and 1400 °C for 30 min.

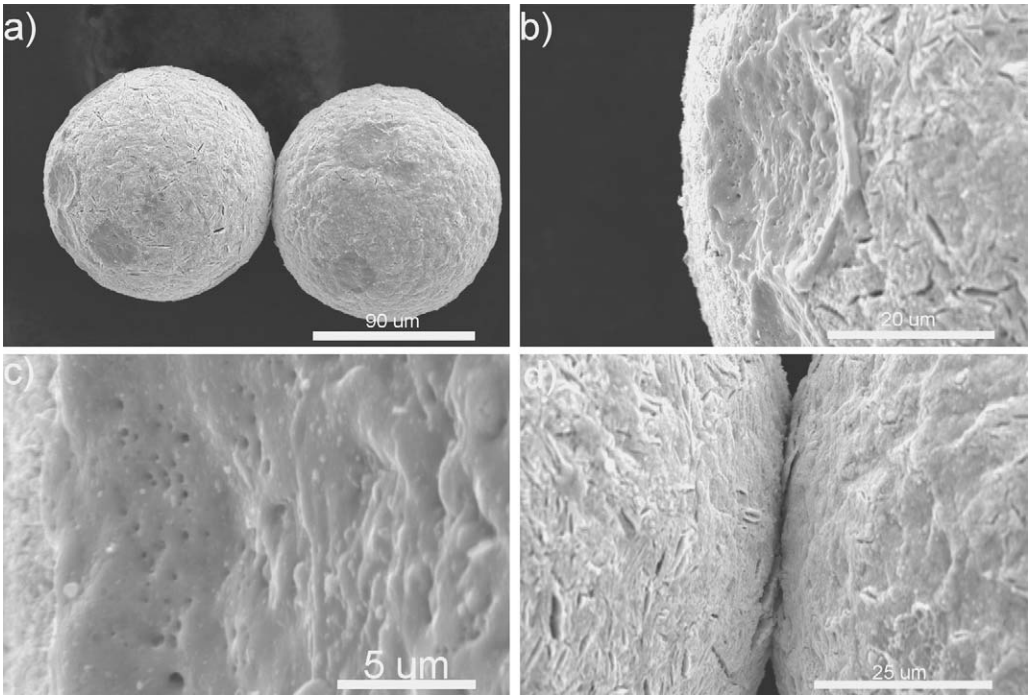


Fig. 5. Neck growth during microwave sintering of WC at 950 °C, 20 min soaking time.

3.3. Analysis of neck growth kinetics

SEM investigation of mono-layer of sintered WC particles for different temperatures and soaking times were made and results are shown in Figs. 5 and 6. Fig. 6(b and c) exhibits classical coin shape contact while Figs. 5(b and d) and 6(d) represent typical contacts observed in the present study.

Analysis of experimental data on isothermal neck growth kinetics [13] established that the exponent in $(x/a)^n \sim Bt$ relations (Fig. 7(a and b)), is in agreement with volume and surface diffusion mechanism, where x – neck size, a – particle radius and B – rate constant. Possible division of neck growth process into two stages is quite apparent (Fig. 7(a)) with neck formation process taking place during heating process at set

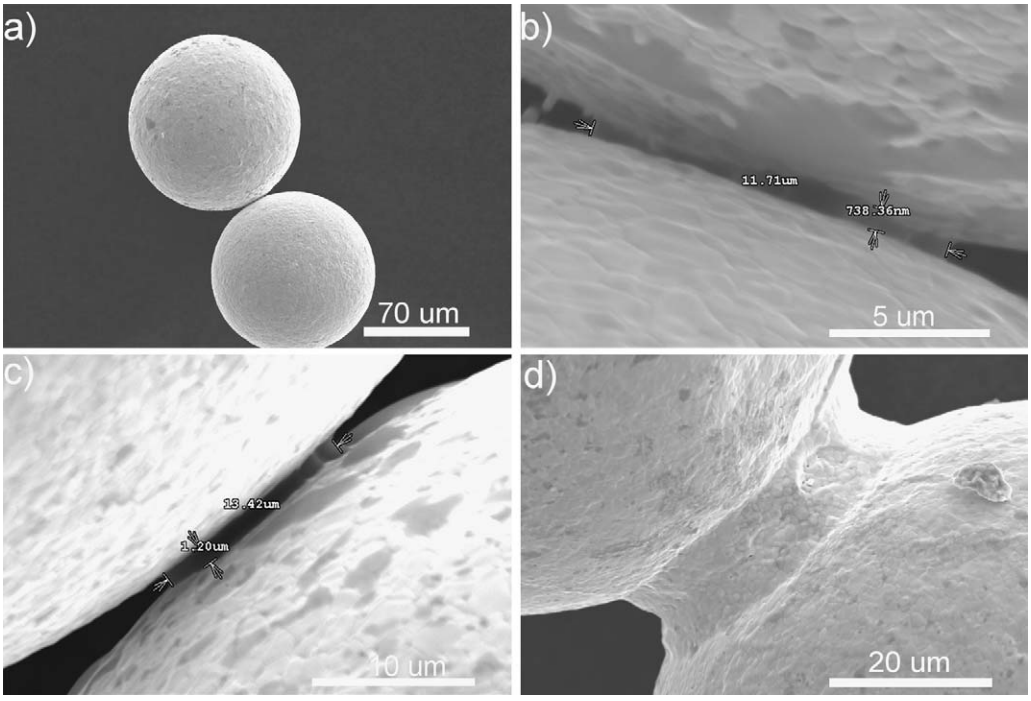


Fig. 6. Neck growth during microwave sintering of WC at 1200 °C (a: no dwell time applied; b: 5 min; c: 15 min; d: 120 min).

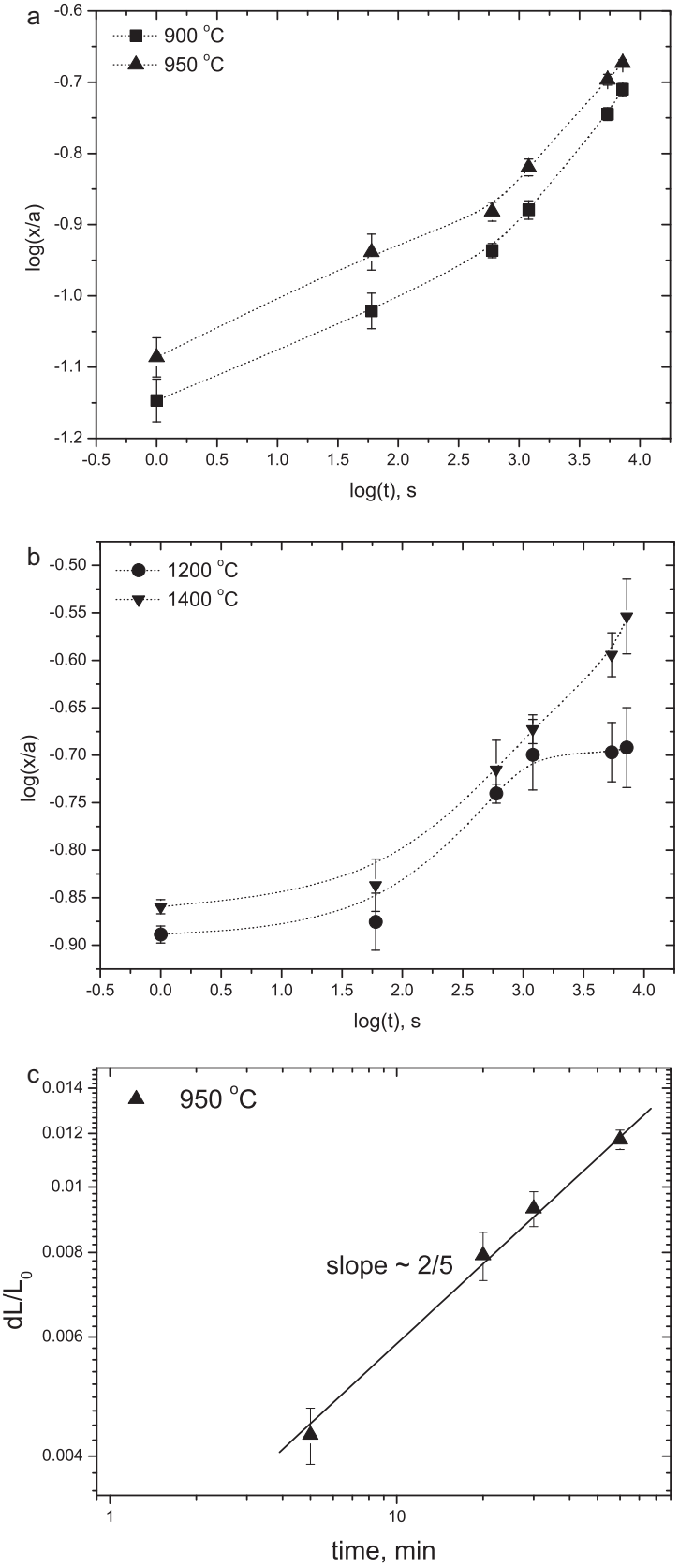


Fig. 7. Time dependence of neck growth during microwave sintering of tungsten carbide: (a) neck growth at 900–950 °C; (b) neck growth at 1200–1400 °C; (c) rate of center approach of WC spheres in contact at 950 °C.

temperatures and ends at short soaking times with $n \sim 15$, else this stage may be explained by simplifications adjusted in sphere-to-sphere model used [14]. Anyhow this division is clearer while comparing lower to higher temperatures as for late (Fig. 7(b)) initial stage, which includes neck formation, is shorter. It occurs due to additional exposure to microwave power during ramping to higher temperatures while the total value of absorbed power at the start of soaking period is almost the same as for short period (up to 5 min) of soaking at lower temperatures.

Once stage of neck formation is completed, diffusion derived process of neck growth starts. Analysis of neck growth process for 900 and 950 °C introduces values of invert slope equal to 4.8 and 5.2, respectively. These values are in good agreement with the value (5.0) that is usually reported for volume diffusion [18]. Moreover, a decrease in center–center distance of spheres was observed (Fig. 3(c)), indicating that volume diffusion must have taken place [18]. These data for WC spheres are shown on Fig. 7(c). The relationship observed corresponds to $(\Delta L/L_0) \sim t^{2/5}$ time dependence that was previously reported for volume diffusion of copper [18].

For final temperature intervals of 1200 and 1400 °C, values of 7.0 and 7.2, respectively, show that surface diffusion is predominant mechanism, as is usually expected for higher temperature range [20,21]. No decrease in center–center distance of spheres was observed for both temperatures, typical neck contact for this temperature range is presented in Fig. 3(d). For 1200 °C, after period of neck formation, the neck growth region that corresponds to sintering by surface diffusion is followed by the region of saturation, which is observed only for one temperature, so neck growth kinetics curve looks like typical S-type curve for densification kinetics during sintering process [22]. The region with almost no growth in neck length may be explained by exhaustion of initial driving force (curvature) and while further growth is impossible unless sintering conditions are changed. It could however lead to further neck growth for bigger soaking times, which was previously reported for conventional sintering of metals and ceramics [23]. However, the overall rate of neck growth examined during microwave sintering can be compared with ultra-high heating rate [24], and further growth may be expected for soaking times that are typical for conventional processing but rarely used in microwave sintering [25].

With rise of temperature to 1400 °C after initial stage of neck formation, the neck growth corresponds almost perfectly to surface diffusion. The absence of saturation stage could be explained with rise in soaking temperature which in combination with high soaking times results in further neck growth. Nevertheless values of x/a ratio that we experience during this research are still lower than the critical value of 0.3, where initial stage of sintering process is assumed to end [26].

3.4. Numerical simulation of neck growth kinetics

While analysis of experimental data suggests that surface and volume diffusion to be main sintering mechanisms responsible for neck growth during initial stage of microwave sintering of given powder, it is interesting to estimate the diffusion coefficient responsible for neck growth. It is quite possible that higher temperatures exist at the contact zone as predicted [27], due to relatively higher absorption of electromagnetic radiation at the grain boundaries/surfaces. Thus a partial melting may be possible during microwave sintering of metals [28]. The form of neck growth equation allows ones to estimate effective diffusion coefficient for given sintering mechanism [18,19,29]:

$$\left(\frac{x}{a}\right)^n = Bt, \tag{1}$$

where x/a is the ratio of the interparticle neck radius to the particle radius, B is a rate constant (which includes particle size, temperature and geometric and materials terms), t is the sintering time, and n is a mechanism–characteristic exponent that is dependent on the mass transport process.

In case of volume diffusion controlled sintering, the dependence of neck size x is given by

$$\frac{dx^5}{dt} = B, \tag{2}$$

where

$$B = \frac{40\gamma\delta^3 a^2 D}{kT}; \tag{3}$$

for surface diffusion controlled sintering:

$$\frac{dx^7}{dt} = B_s, \tag{4}$$

where

$$B_s = \frac{56\gamma\delta^4 a^3 D_s}{kT}. \tag{5}$$

In Eqs. (2)–(5), D is the volume diffusion coefficient, D_s is the surface diffusion coefficient, δ is the interatomic distance, a is the radius of spherical particles undergoing sintering, and γ is the surface energy of pore-solid surface.

Let X_0 be the neck size at $t = 0$, integration of Eqs. (2) and (4) yields:

$$\text{volume diffusion}: \quad X = (X_0^5 + Bt)^{1/5} \tag{6}$$

$$\text{surface diffusion}: \quad X = (X_0^7 + B_s t)^{1/7} \tag{7}$$

It is traditionally assumed that X_0 is equal to zero, which reduces Eqs. (6) and (7) to classic $X \propto (Bt)^{1/n}$. Thus, like in this work, the exponent n may be recalculated from the plot of $\log(x/a)$ or $\log(x)$ vs. $\log(t)$. This approach is valid, provided the samples are introduced in the furnace at sintering temperature; either heating to sintering temperature is almost immediate [18]. In the present case, though we introduce samples in the cold furnace, we keep ramping rate high enough to assume that heating stage is small enough to dwell times we apply. However, even with no dwell time applied (Fig. 7(a and b)) the neck is already formed, proving high value of diffusion in case of microwave sintering for given material. Thus using Eqs. (6)

Table 1
Material constants used for computer simulations.

Particle radii	62 μm
Atomic volume	2.59×10^{-29} m^3 [19]
Surface energy	2.45 J m^{-2} [19]

and (7), and experimental values of X_0 obtained in this study, we may estimate effective value of diffusion coefficient by finding correct value of rate constant B, which includes diffusion coefficient. Values of δ and γ are taken from elsewhere [19], while k is the Boltzmann constant, while a is particle radius, reported earlier (Table 1).

Values of diffusion coefficients obtained in this manner is 7.16×10^{-13} and 3.41×10^{-8} m^2 s^{-1} for 950 and 1200 °C respectively, with simulation of neck growth are presented in Fig. 8. It is obvious that there is some mismatch on the initial stage of neck growth, but with increase in soaking time (Fig. 8(a)) numerical simulation fit experimental data perfectly. But where value of invert slope "5" should correspond to volume diffusion, the diffusion coefficient revealed by

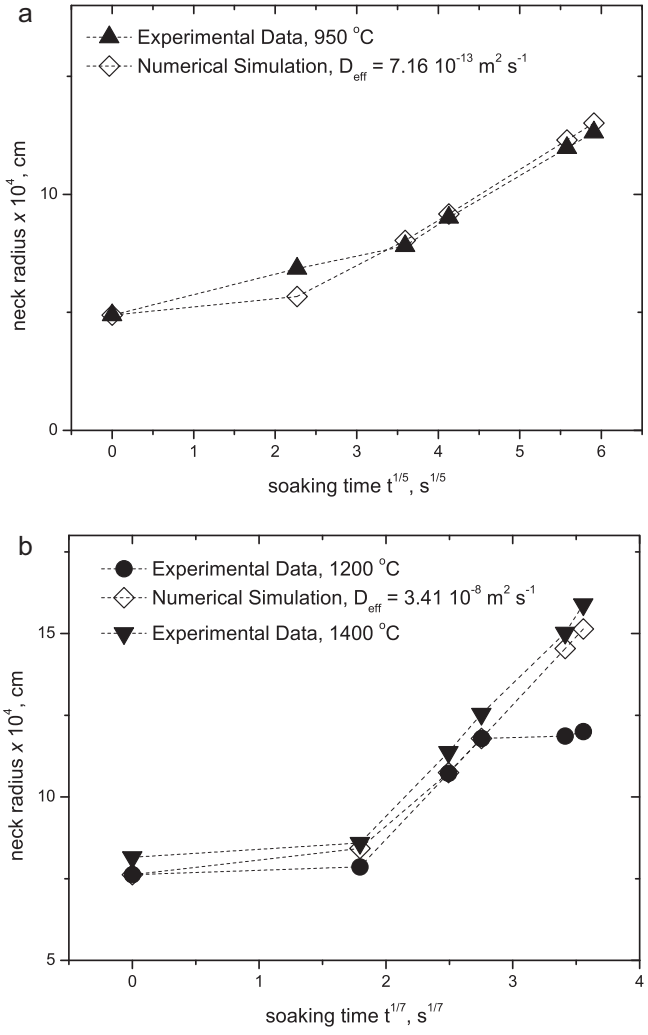


Fig. 8. Comparison of experimental and theoretical values of neck size during microwave sintering at: (a) 950 °C; (b) 1200 and 1400 °C.

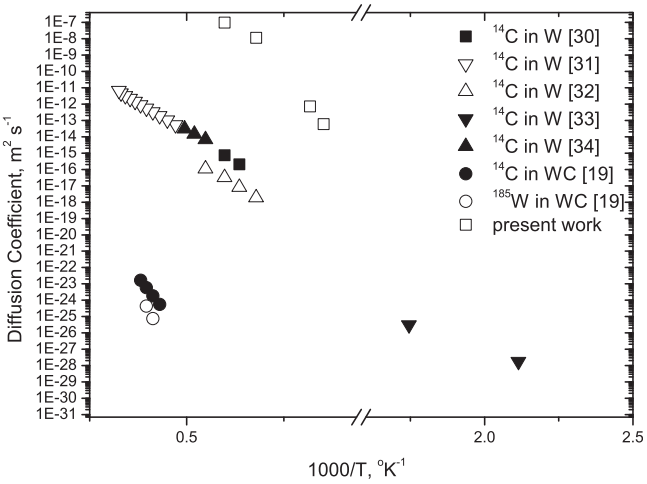


Fig. 9. Diffusion coefficients of W and C in W and WC vs. reciprocal temperature.

numerical simulation is anomalously high as compared to diffusion coefficients of W, C in W and WC [30–34] (Fig. 9). Furthermore for 1200 °C (Fig. 8(b)) diffusion coefficient is even higher as well as there should be no saturation stage during neck growth. In fact, data for 1400 °C (Fig. 8(b)) lie perfectly on the same slope. Simulation of neck growth process allows us to compute effective diffusion coefficient for all processing temperatures, and the inverse slope in Fig. 5 gives activation energy of neck growth process as 69.18 °kJ mol^{-1}. This is significantly lower then any data on diffusion in this system at given temperature interval [19,30–34]. This fact, alongside with value of diffusion coefficients may show that for this case mass transport was either supported by additional driving force [7], or it is due to the local overheating (Fig. 5(c)), taking into account that at contact areas between particles value of electric field maybe significantly higher then generally in volume of resonant cavity [27]. Else, it may be supported by small amount of liquid, small enough to enhance the neck growth process, while being insufficient enough to refer sintering as liquid phase sintering. But while, in this case no binders or susceptors were used, the formation of the liquid itself may be possible only due to high gradient in electro-magnetic field and creation of eddy currents on particles' surface. To support probability of presence of liquid phase the works on initial stage during liquid phase sintering for conventional sintering [35,36] predicted that neck growth should obey almost the same laws as solid state sintering, with sintering rate exponent n equal to 5 and 6 (for bigger soaking times). Nevertheless, though formation of liquid phase during initial stage of microwave sintering may be possible, as it is supported by bigger diffusion coefficients and lower activation energies. The question of experimental evidences of liquid phase should be addressed in further work, mainly focusing on heating stage of the sintering process, by changing the frequency of microwave source to ensure pure microwave nature of this effect.

4. Conclusions

Model experiments on initial stage of microwave sintering of binderless tungsten carbide spheres have been carried out.

Pure microwave heating was used during sintering experiments in 2.45 GHz multimode applicator. Investigation of neck growth process showed that neck growth process may be divided into two stages, first that could be governed by non-conventional diffusion mechanisms. Sintering data for WC spheres on the second stage at 900, 950 °C are in good agreement with volume diffusion mechanism. For higher temperature surface was found as predominant diffusion mechanism. Finally, numerical simulation of neck growth process revealed anomalous diffusion coefficients – 7.16×10^{-13} and $3.41 \times 10^{-8}\,m^2\,s^{-1}$ for 950 and 1200 °C respectively, and activation energy of mass transport of 69.18 kJ mol^{-1}; those are not associated with conventional sintering process and may be caused by either local overheating or even by formation of liquid phase during neck formation/growth process.

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