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Neck growth kinetics during microwave sintering of nickel powder

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ABSTRACT

Model experiments on initial stage of microwave sintering of nickel powder showed anomalous neck-growth rate during isothermal soaking, which is not the case for conventional sintering. Neck growth was determined as a function of time. Values for the neck growth exponent in the neck growth equation, $(x/a)^n = Bt$, of 5.2, 5.4, 5.8, and 5.9 were found for within the temperature range 700–950 °C, respectively.

The evidences of formation of liquid phase during microwave sintering have been revealed, that may support enhancement of mass transfer during sintering process. The activation energy of 48 kJ mol^{-1} was found for microwave sintering of nickel, according to sphere-to-sphere model. Value revealed is significantly lower then values for conventional sintering (136 kJ mol^{-1}), and is on same level with activation energy for diffusion of metals in liquid state. An explanation and analysis of this phenomenon has been attempted.

1. Introduction

Microwave sintering is relatively new method for processing of ceramics and metals and is generally associated with high heating rates and volumetric heating [1]. Microwave sintering ensures considerable time and energy saving [2], and therefore is viewed as one of most perspective sintering techniques in material processing [3]. Thus, it is of great importance to establish relationships those are acting during microwave sintering process of powder systems. Therefore metal powders were used for various scientific research on modeling of heating [4], shrinkage kinetics [5], microstructure evolution during sintering of metal powders in single-mode cavities [6].

However, most of these works were dealing with either heating of metals [7] or later stages of sintering [8], those are usually similar to those for conventional sintering [9]. The results that have been recently revealed on initial stage of microwave sintering [10], confirmed that during microwave heat treatment of metals the neck formation process may be started during heating, or soaking for few seconds in case of processing in pure *E* or *H* field [6]. Later is generally attributed to intense interaction of eddy currents on particles' surface with surface layer [6]. This may lead to ignition of microplasma discharges [11], or even to local melting [12]. For ceramics enhancement in diffusion was described for ionic conductors in terms of pondermotorive force model [13]. But from the point of view of sintering process, the origin of overall enhancements during microwave sintering processes is therefore still questionable, in this terms works that deal with exploration of sintering mechanisms are generally required.

Therefore work using initial sintering stage models were successfully used for research on novel sintering processes like Spark-Plasma Sintering [14], as well as microwave sintering [10], revealing possible mechanism behind enhancement of sintering processes.

In the present work, study of neck growth kinetics by exploiting classical sphere-to-sphere model [10,15–17] was proposed as model experiment for studying initial stage of microwave sintering of spherical shaped nickel powder. Secondly, investigations were undertaken to formulate hypotheses about the mechanisms controlling the initial stage of microwave sintering and evaluate the effective diffusion coefficient on the basis of experimental data obtained.

2. Materials and methods

For model experiments in microwave sintering spherical shaped gas-atomized nickel powder was used (IPMS, NAS Ukraine). Particle's size distribution (Mastersizer) and EDX techniques were applied to characterize initial powder.

A number of neck growth kinetics experiments were conducted using sphere-to-sphere approach [15–17], in order to investigate diffusion mechanism that control initial stage of microwave sintering. Thus a monolayer of free packed nickel particles was placed on microwave transparent mulite substrate, which was then placed into mulite insulator which is named as sample in Fig. 1, number of spheres on the plate

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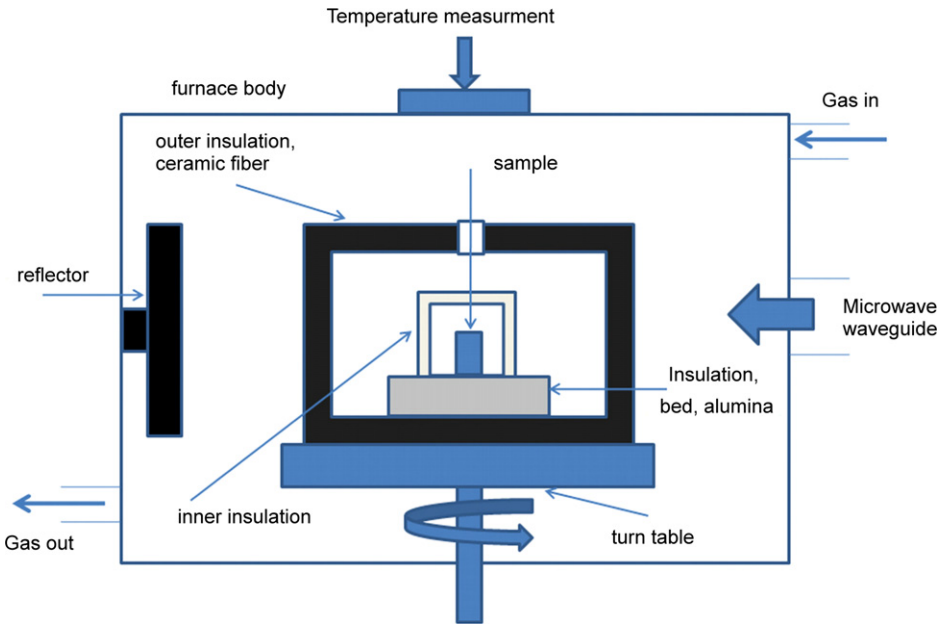

Fig. 1. Schematic diagram of microwave set-up used in the present study.

was kept roughly the same for every run, as dimensions of insulator used (hollow cylinder with inner diameter of 20 mm), were used to restrict a number of particles used. The sample was placed on alumina plate and covered with alumina-zirconia insulator to insure minimal temperature losses during microwave heating. Sintering experiments were held using 6 kW, 2.45 GHz multimode microwave cavity, detail information on experimental set-up is provided elsewhere [7,10]. No additional susceptors were used in the experimental set-up, so that the heating was pure microwave heating. Inert atmosphere was maintained during sintering process by ultra high purity (UHP—99.999%) nitrogen. Throughout the sintering, nitrogen gas flow was maintained at 2 L min^{-1}.

The temperature was monitored using infrared pyrometer Raytek MA2SC (working temperature range 350–2000 °C) and recorded in situ by a computer. Heating to set temperature with same heating rate was made possible by controlling the power of microwave generator (Fig. 2). After sintering temperature was reached microwave generator power level was suitably reduced to get constant temperature for soaking period, and the isothermal holding was applied. After sintering, the microwave power was switched off and the samples were allowed cooling with the furnace.

After cooling, batch of sintered spheres was examined by SEM (Hitachi S-3500N) to investigate neck's size. To ensure validity of measured data, every sintering run was repeated three times, the number of necks measured for every point per run exceeded 10, an average data on neck size will be used below 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, $m \geq 10$.

3. Results

For sintering experiments narrow particle size distribution is desirable as it allows observation of size changes during sintering process. Nickel powder used in these experiments was characterized by monomodal particle size distribution with mean and median size of 255 and 267 μm (Fig. 3).

Initial powder had a spherical shape (Fig. 4), the EDX (not shown) confirmed nickel as main component, with some oxygen is present (0.4 wt.%) mainly as surface oxide layer.

Heating rate to set temperature was chosen as 180 °C min^{-1} (Fig. 2), so that soaking for all temperatures would be performed at same microwave generator power level of 800 W. After soaking time was applied and microwave power source has been turned off, the sufficient drop in temperature of sample was observed, after reaching to 400 °C mark, the rate of gas flow was increased up to 4 L min^{-1}, and temperature gradually decreased by 20–30 °C min^{-1}.

The substrate used during experiments was made from microwave transparent material and remained much colder then metal powder. Minor variations in microwave power level were

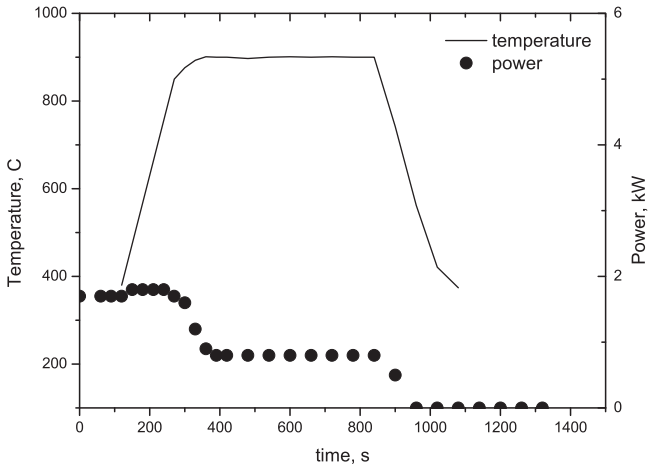

Fig. 2. Thermal profile of nickel spheres during sintering at 900 °C for 5 min.

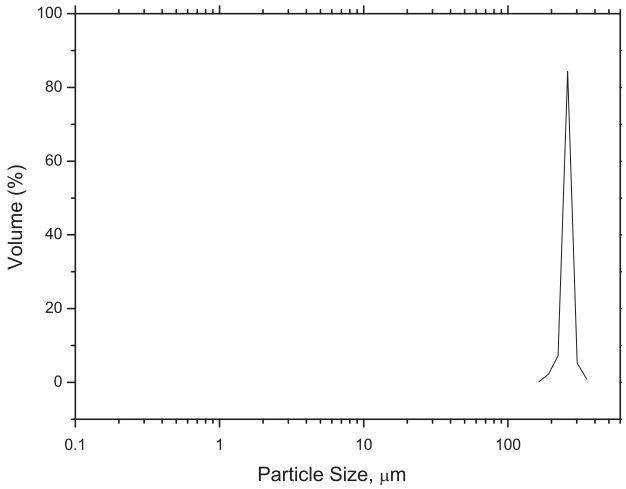

Fig. 3. Particle size distribution of nickel powder.

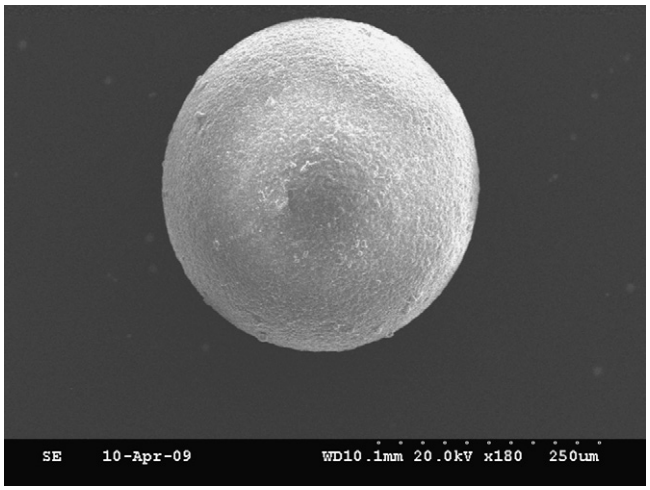

Fig. 4. SEM image of nickel powder used in the present study.

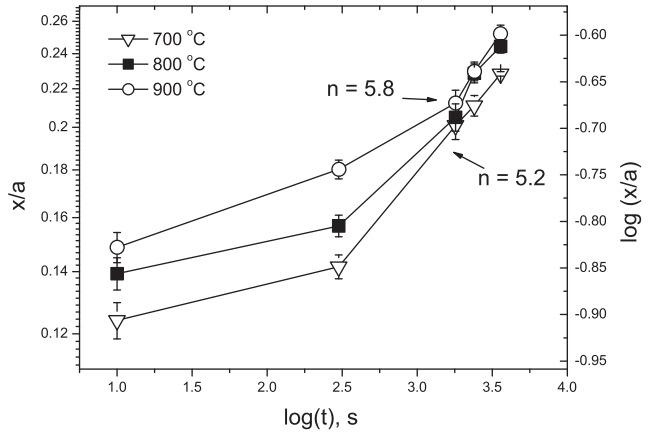

Fig. 6. Time dependence of neck growth during microwave sintering of nickel at 700–900 °C.

manually made if there was a drop in temperature for more than 10 °C from the set point. The pyrometer used in current investigation was calibrated on melting points of copper and nickel samples and accuracy provided in sintering temperature range used was ±5 °C.

Data of SEM (Fig. 5) and optical microscopy for nickel spheres during initial stage of microwave sintering were analyzed using Kuczynski's approach [15]:

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

where x is the neck radius, a is the sphere radius, t is time, and B and n are constants.

Hence, neck growth is presented by the graph in Fig. 6. The invert slopes of the best-fit straight lines for the data points at 700–900 °C are 5.2, 5.4 and 5.8 respectively. These value were obtained by a least squares analysis of the data, using an equation of the form $\log x/a = \log B + 1/n \log t$.

In contrast to previous results during microwave heating of copper powder in single-mode cavity [6], where neck formation and growth process was predicted to last ~20 s, neck growth was not formed during short exposure to microwaves, and was not detected bellow 600 °C. Even at 600 °C the overall number of necks in the system was small, and while short soaking times were applied the number of necks measured was barely exceeding 10. With rise in processing temperature the actual number of necks being formed increases. The size of interparticle necks also increases with soaking time applied.

During the course of making measurements, several interesting phenomena were observed. Thermal faceting of particle's surface was quite prominent especially after 120 min of sintering. X-ray analysis and EDX of nickel powder (not shown) indicated the absence of oxides on powder surface. This may indicate that during microwave heat treatment in nitrogen the surface ion milling occurred, as it was previously reported for some nitrides and ceramics [18].

Another interesting feature was formation of donut shaped neck (Fig. 5(a)), with entirely different surface inside and outside the

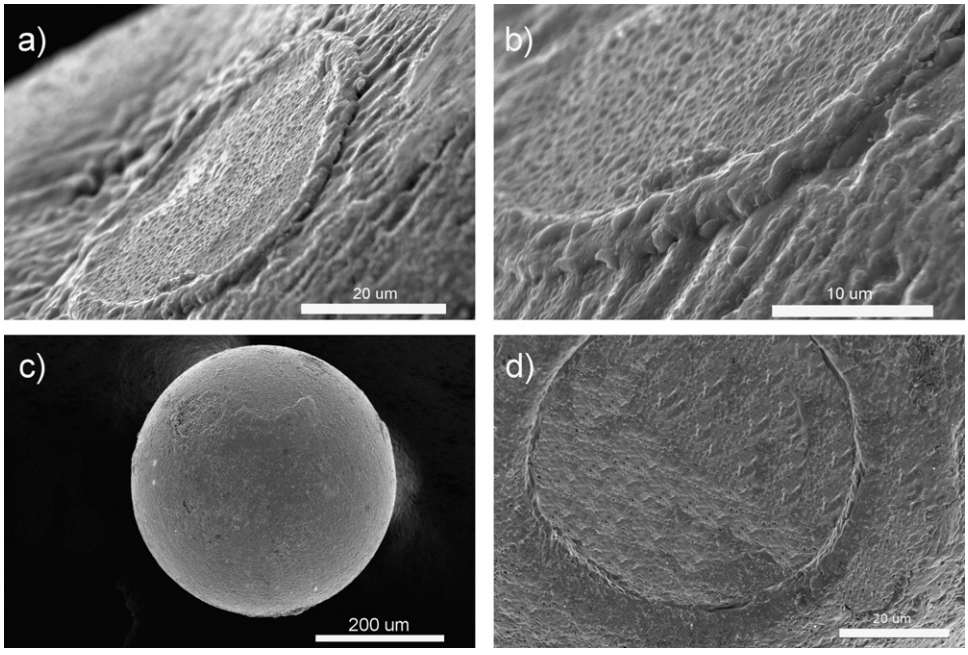

Fig. 5. Neck growth during microwave sintering of Ni: (a) 700 °C × 30 min (general view), (b) 700 °C × 30 min (neck zone), (c) 700 °C × 30 min (typical particle with necks), (d) 700 °C × 30 min (coin-type neck).

Table 1
Experimentally determined sintering rate exponents for sintering of nickel.

Type of sintering	Temperature, °C	Sintering rate exponent, n
Microwave sintering [current work]	700	5.2
Microwave sintering [current work]	800	5.4
Microwave sintering [current work]	900	5.8
Conventional sintering [20]	1400	4.7–5.4
Conventional sintering [21]	1000–1300	5.2–5.8

neck zone (Fig. 5(b)). What is more interesting is that the value of neck radius was almost the same as for other coin-shaped necks (Fig. 2(c,d)) for given time and temperature interval.

4. Discussion

4.1. Reliability of data

The standard deviations of x/a measurements are shown by the brackets in Fig. 6. These deviations are of the order of 7–10%. Such magnitudes are due to a) the distribution in spheres sizes, b) non-circular shape of some necks and c) to normal statistical variations. Wilson and Shewmon [19] pointed out that a 20% variation in x/a values is to be expected for a given set of sintering conditions and spheres of identical diameter.

4.2. Neck growth kinetics

Sintering rate exponents, determined as inverse slope from log/log plots of Fig. 6 are summarized in Table 1. The value of the exponent is in complete agreement with values reported by Pranatis [20] and Elliot [21] for conventional sintering of nickel wire compacts and sphere-to-plate experiments. According to theory, these values of the exponent, between 5 and 6, indicate either volume or grain-boundary diffusion as the operative material transport mechanism [22].

Pranatis and Siegle [20] postulated a volume diffusion mechanism based on their observation, of a lack of an effect on neck growth of the presence or absence of grain boundaries, and proximity to values reported in the literature of their calculated values for self-diffusion coefficients and the activation energy for diffusion. Furthermore, they found agreement with Herring's scaling laws [23] for a volume diffusion mechanism.

Elliot and Munir [21] also reported a volume diffusion mechanism for pure nickel powder, having showed that it would be also the case for Ni–Al alloy. But if we compare previously reported results with those for current investigation, (Fig. 7), one may notice some major differences. First, there is an apparent two stage process, which was previously reported for copper powder [10], with first stage responsible main for neck formation and is not governed by conventional sintering rate laws. Values of inverse slope of 12–18, cannot be attributed to any diffusion governed mechanism, therefore they indicate that there is no substantial neck growth occurs on this stage taking into account that we are talking about process which lasts for up to ~100 s. After neck formation process is complete, the neck growth process starts with almost same slopes values that are for conventional sintering.

Second, there is huge difference in temperatures and soaking times (up to 10 times faster for microwave sintering case) applied. While temperature measurements for microwave sintering process is being well argued [24], no thermocouple or susceptors, those are responsible for changing electromagnetic field patterns and hence temperatures measurements errors, were used in present study. Infrared pyrometer used in present study was calibrated on melting temperatures of copper and nickel samples, but the nature of microwave induced heating of metals suggests that temperature being monitored is still an average value for certain system. However, it should be also noted that for temperatures higher then 800 °C, second pyrometer was used for reference. For present research temperature factor seems to be significant during neck formation stage (Fig. 6). With increase in temperature the size of neck being formed increases, while after neck formation process being completed, the neck growth process seems to take place with identical neck-growth rate. There is though a slight rise in neck-growth rate exponent value from 5.2 to 5.8, from 700 to 900 °C respectively, these values seem to be the same as for conventional sintering process [20,21].

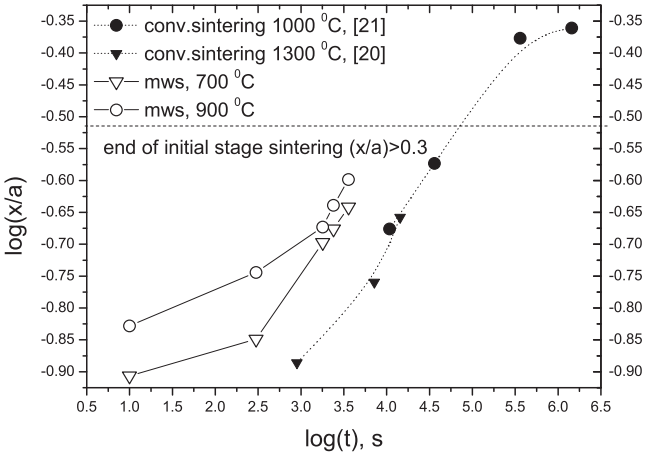

Fig. 7. Neck growth kinetics during microwave and conventional sintering [20,21] of nickel powder.

As for significant change in processing time required for neck to grow to given value, it may be noted that a change in scale ~10 between microwave and conventional sintering data seems to be the main question. With both processes process governed by $x/a \sim Bt^{1/n}$ equation the term for rate constant B seems to significantly change in order to compensate decrease in processing time. Rate constant B is directly proportional to value of the apparent diffusion coefficient D [22]:

$$B \sim \frac{D\gamma\delta^3}{kT}, \quad (2)$$

where D—diffusion coefficient, γ—surface tension, δ^3—atomic volume, k is Boltzmann constant and T is temperature.

It is trivial to conclude that change in diffusion coefficient will be proportional by $(t_1/t_2)^n$, and for given t_1/t_2 ratio being 8–10, with t_1 corresponds to conventional and t_2 to microwave sintering, change in diffusion coefficient should be by 10^4–10^5 orders of magnitude. For metal like nickel such change in diffusion coefficient would mean the diffusion rates on same level for those for liquid nickel $\sim 10^{-7}$ m^2 s^{-1} [25]. The precise value of diffusion coefficient may be calculated by means of numerical modeling and may be considered as further step in research, but the effective value of diffusivity should be of order of 10^{-7} m^2 s^{-1}. This fact, alongside with donut-type neck structures, those are quite common for initial stage of liquid phase sintering, should be convenient enough to discuss the initial stage of microwave sintering as the one with some small amount of liquid introduced during neck formation/growth process.

Unlike previous works on copper [6] where small size of particles was used and heating was caused by Joule heating, metal like nickel absorbs microwaves not only as conductor via surface induced eddy currents [12], but also by magnetic permittivity. Even though it would have the real impact on heating process only up to the Curie point (631 K) [26]. Therefore at temperatures used in current study, the high neck-growth rate may be explained in two

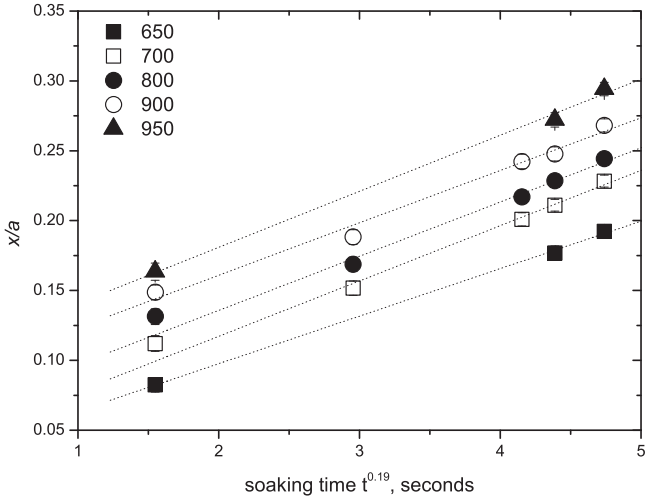

Fig. 8. Kinetics for the neck growth for nickel spheres during microwave sintering.

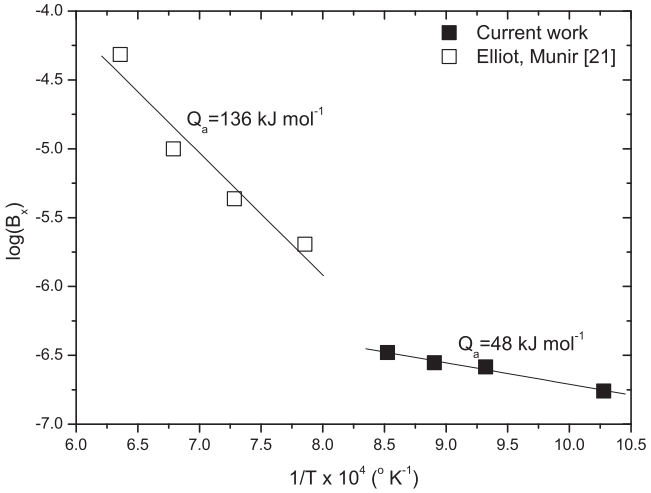

Fig. 9. Arrhenius plot of $\log B_x$, B_x—rate constant, versus $1000/T$ based on data of present investigation.

ways. From one hand, the overall variation of electromagnetic field in contact (neck) region is high enough [27] to transform energy of microwave field into heat and hence form short-term melt in the neck zone. From the other hand, the microplasma discharges between particles may occur, as it was previously reported during microwave processing of powdered metals [11,12], and thus cause partial melting of powder. In any case the amount of liquid introduced is not big enough, as we would experience other structure of necks.

It should be noted that the analysis of Courtney for initial stage of liquid phase sintering [28] deals with small amount of liquid introduced to the system of two spherical particles and the sintering rate exponent is predicted to be 5. The analysis also predicts that if no liquid introduced to the system, the sintering by two spheres model would be almost identical as for solid-stage sintering by volume diffusion and overall equation form (the value of kinetic term B) would differ only by 2π. Moreover the change of neck growth exponent predicted in this model is expected from 5 to 6 [28] with an increase of processing time, which is in good agreement with results of current investigation.

4.3. Activation energy of neck growth process

In order to more closely relate results of this investigation with those previously reported [20,21] for conventional sintering, steps where taken to obtain rate constants (Eq. (2)) and associated activation energy for diffusion. The data of Fig. 6 were replotted in Fig. 8 as x/a versus $t^{0.19}$. Best-fit straight lines were drawn from the origin through the data points. From the slopes of these lines, values were obtained for B as a function of temperature. The value for present work was calculated neglecting first points for 700–900 °C, and therefore was determined by the least squares analysis of the data mentioned earlier. Only 3 points were obtained for 600 and 950 °C, those, it was assumed, uniquely determined value of B at that temperature. The inclusion of these values for the quantitative determination of an activation energy is rather tenuous. However, as shown in an Arrhenius plot to be discussed below, the proximity of the resulting rate constants to the straight line connecting the more firmly established values at 700–900 °C justifies their use.

Using Kuczynski's analysis for volume diffusion mechanism [15], and taking into account Courtney's analysis [28], the rate constant for sintering will be related to B_x by $B^{1/5} = B_x$. Thus, a plot of the logarithm of the fifth power of the experimentally determined B_x values versus $1/T$ should give a straight line with slope is $-Q/R$, where Q is the activation energy for diffusion and R is the gas constant, such plot is shown in Fig. 9. An activation energy for present case of 48 kJ mol^{-1}, was obtained by least squares analysis for microwave sintering of nickel spheres. The data for conventional sintering of nickel wires by Pranatis and Siegle [20] and spheres to plate Elliot and Munir [21] are also included. For later an activation energy of 136 kJ mol^{-1} has been obtained and concluded volume diffusion to be main sintering mechanism, while Pranatis and Siegle obtained 331 kJ mol^{-1} for sintering of wires in hydrogen for 3–400 h, as compared to approximately 286 kJ mol^{-1} for the self-diffusion of nickel determined by other means [29,30]. Thus the magnitude of activation energy for diffusion for microwave sintering is anomalously low, comparing even to those for grain-boundary diffusion mechanism 108 kJ mol^{-1} [20], and is on the same level with diffusion of nickel in liquid state 38–42 kJ mol^{-1} [31,32].

5. Conclusions

Initial stage of microwave sintering of nickel powder showed anomalous neck-growth rate during isothermal soaking. The evidences of formation of liquid phase during microwave sintering of nickel powder have been revealed, that may support enhancement of mass transfer during microwave sintering process. The activation energy of diffusion processes during initial stage of microwave sintering for nickel powder has been calculated as 48 kJ mol^{-1}, value of effective diffusion coefficient has been shown to be on level of 10^{-7} m^2 s^{-1}, which is on same level with diffusion coefficient of liquid nickel.

Acknowledgements

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jallcom.2010.10.042.

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