Coarsening, Densification, and Grain Growth during Sintering of Nano-sized Powders

– A Perspective

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ABSTRACT

Sintering is one of the main approaches, among limited options, for building bulk nano materials from bottom up. A primary challenge of sintering nanosized powders is to control grain growth while achieving full densification. Considerable literature is now available in the search for unique mechanisms that could assist in achieving densification with minimum grain growth. It is critical to understand the detailed mechanistic steps, in order to design processes that might lead to bulk nano materials with maximum density and minimum grain size. Using experimental data of sintering nanosized tungsten carbide and tungsten powders, as well as selected data on other materials in the literature, this article examines the unique characteristics of nano sintering, including the driving forces, kinetics, and intertwined processes of neck growth, coarsening, densification, and grain growth. When the density of the powder compact of nanosized particles are very low, coarsening of particles is responsible for most of the observed initial growth of grain sizes as well as densification. Because the mechanism of the initial coarsening depends on surface diffusion, surface diffusion thereby contributes to densification indirectly. Although the initial grain growth is only a small fraction of the total grain growth that occurs by the completion of sintering, it is the most critical part of grain growth, determining whether the grain size of the material can be controlled within the nanoscale regime.

1. Introduction

Sintering is probably one of the oldest fabrication methods known to mankind, particularly in the fabrication of pottery and ceramics. It is also one of the main and few approaches for building bulk nano materials from the bottom up. A general, but primary, challenge of sintering nanosized powders is to control grain growth while still achieving full densification. Considerable literature is now available in the search for unique mechanisms that can assist us in developing the means to achieve full densification with minimum grain growth. It is critical to understand the detailed mechanistic steps involved, in order to design processes that might lead to bulk nano materials with maximum density and minimum grain size.

The science of sintering has been extensively studied and documented. The classic models of sintering were developed by Coble and Kingerey [1, 2]. Later, several diffusion mechanisms were incorporated into the sintering models [3], and later, Ashby presented sintering maps to detail the relationships among different active sintering mechanisms versus temperature and their relative contributions to densification during sintering [4]. However, most of the existing sintering models are based on two-sphere geometric models, and are focused on microstructural changes, i.e. pore closure and grain growth, during isothermal holding. However, the dependence of the driving force of sintering on the evolution of particle sizes and morphologies during densification, in addition to simultaneous effects of different diffusion mechanisms, render such predictions on the sintering behavior of real powder compacts inaccurate. This is especially an issue when considering the sintering of nano-sized particles.

In the last two decades, the improvement in computing capabilities has been applied to gain further insight into sintering behavior [5, 6]. Numerical simulations have a clear advantage over two-sphere geometric models because far fewer assumptions are necessary. Yet, the capacity of numerical modeling is still limited with regard to multi-particle models that involve all sintering mechanisms, diffusion processes and multiple stages of densification and grain growth [7, 8, 9]. Further, the rapid development of processes since the 1990s for synthesis of nano-sized powders has brought new opportunities for sintered products from nano-sized powders, as well as new challenges. While processing these nano-sized powders via sintering, keeping grain size within the nanoscale has proven to be a very difficult challenge due to their higher surface energy, which drives both consolidation and grain growth. Researchers developed not only advanced sintering processes in order to control the grain growth, but also gained new knowledge by investigating unique features of nano-sized powders and their response to sintering. These investigations have included topics such as the reduction of sintering temperature [10], the relative contribution of solid state sintering during the liquid phase sintering process [11], and the role of particle rearrangement in the early stage of sintering [12, 13]. However, it suffices to say that the challenge to controlling grain growth during sintering of nano-sized particles remains, and a thorough understanding of the complex processes at work during nano sintering continues to be insufficient.

In the past several years we have investigated sintering of nano tungsten and tungsten carbide powders to achieve full densification, while minimizing grain growth to obtain nano-sized grains in final sintered products. The purpose of this paper is to provide a perspective on the sintering behavior of nano-sized powders, and the intertwining relationships between coarsening of particles, densification, and grain growth by grain boundary migration. To be clear, "coarsening" is defined here as the increase of particle sizes at the early stage of sintering via inter-particle mass transport mechanisms rather than grain boundary migration. This perspective is based on both our experimental data and reporting in the literature. One of the main findings is that although nano sintering follows the same thermodynamics that govern the driving force of sintering as a function of the particle sizes, but the coarsening of nano-sized particles, which begins at very low temperatures, plays a more dramatic role during nano sintering than during conventional sintering. The coarsening of particles is a primary mechanism at the early stage that leads to both densification and an increase in average grain size. During this initial stage of sintering, the coalescence and rearrangement of particles reduces the coordination number around pores, and alters the balance of surface tension around pore surfaces, which drives the closure of pores. The coarsening that occurs during the initial stage of sintering is a critical step that determines the grain size of the sintered product with respect to its capacity to retain nano-scale characteristics after full densification. The densification and grain growth processes during the later stages of sintering are similar to those of conventional sintering when the relative density is greater than 90%. In short, understanding the details of the processes of coarsening, densification, and grain growth, and the roles of different diffusion mechanisms, is essential for designing processes for nano-sintering. The details of these findings are elaborated in this paper.

2. Experimental observations of nano-sintering

In order to understand the micro scale or nano-scale mechanisms, we begin with macro-scale observations of the sintering of nano-sized powders. Figure 1 shows the densification of nano-sized cemented tungsten carbide WC-Co and nano-sized tungsten (W) as a function of temperature [14, 15]. These samples were heated to the temperatures and then cooled down immediately without holding at the temperatures. Figure 1 compares the densification of different sized powders. It shows that the entire densification curve is shifted to the lower temperature range with a decrease of particle sizes. The finer the initial particle size, the lower the temperature that is required to achieve a given sintered density. Or, at a given temperature, nano-sized powders can be sintered to a higher density than can micron-sized powders. These results suggest that the sinterability of nano powder is significantly enhanced. Note that the starting green density of nano tungsten powder in Fig 1 (b) (e.g. particle size 52, 57 and 36nm) is lower than that of submicron tungsten powder (e.g. particle size 260nm). The characteristic of low green density of nano powder necessitates an extended initial or early stage of nano-sintering.

Insert Figure 1

Fig. 1. Densification curves as a function of temperature: (a) nano-sized cemented tungsten carbide (WC-Co) [14], (b) nano-sized tungsten [15].

Figure 2 shows the grain growth of nano WC/Co and nano tungsten powders during isothermal sintering, as functions of the temperature and isothermal holding time [16, 17]. It shows that the grain size of these materials grew drastically to beyond the nano-scale. Hence the material after sintering was no longer a nano-material. More importantly, it is noted that the first data points with no holding time in each of these examples show that the grain size has increased multiple times larger than their initial grain size or particle size, which suggests substantial grain growth occurred during heating to the sintering temperature. Therefore, the grain growth during the heating phase necessitated further examination.

Insert Figure 2

Fig. 2. Grain growth during sintering as functions of the temperature and isothermal holding time for: (a) nano tungsten carbide (WC-Co) sintering at 1200 ºC and (b) nano tungsten powders.

Figure 3 shows the grain size changes during heating from ambient to sintering temperature for nano-sized WC-Co and W [16, 17]. The figure demonstrates that grains grow rapidly as the temperature increases through a given temperature range. An exponential growth takes place, after an initial slow growth process at temperatures below 1100 °C for nano-WC-Co, and 950 °C for nano-W. Note that the onset temperature of the exponential growth may vary depending on the specific material and the initial particle size of the powder. Figure 3 also shows that, at the point that the sintering temperature is reached, the grain size can already exceed the nano-crystalline material range. This result suggests that if the objective of sintering is to achieve nano-scaled grain size in the fully or near-fully dense bulk material, understanding and controlling grain growth during the heating stage is essential. The latter stage of grain growth during isothermal holding is no longer relevant if the grain size at the start of the isothermal holding is already too large to be characterized as nano-sized.

Insert Figure 3

Fig. 3. Grain size changes during heating from room to sintering temperature for nano-sized WC-Co (a) and W (b).

3. Fundamentals of nano-sintering

In order to understand the intertwined processes of densification and grain growth, we turn to the fundamentals of sintering, and examine whether the same principles and rules that govern sintering micron-sized particles apply to nano-sized particles. The thermodynamic driving force σ for sintering can be expressed using the following equation:

$$\sigma = \gamma\kappa = \gamma\left(\frac{1}{R_1} + \frac{1}{R_2}\right) \tag{1}$$

where γ is specific surface energy, κ is curvature, and R_1 and R_2 are the principle radii of curvature of a particle surface. It can easily be shown that the driving force for sintering would be two magnitudes higher when the particle size is decreased from 1000 nm to 10 nm, which enhances the sinterability of nano powders. In addition, it has also been shown that the specific surface energy γ increases with decreasing particle size in the nanometer scale [18], which further contributes to enhance the sinterability of nano powders.

The particle size also plays a role when considering lowering the sintering temperature in the attempt to reduce grain growth, since melting point is a function of particle size [19]. Equation (2) and Figure 4 show that the melting point of the material decreases rapidly when the particle size is less than 20 nm.

$$T_m(d) = T_m(\infty)exp\left[-\frac{2S_m(\infty)}{3R}\frac{1}{(d/d_0-1)}\right] \tag{2}$$

where $T_m(\infty)$ is the bulk melting temperature; $S_m(\infty)$ is bulk melting entropy; R is the gas constant; d is particle diameter; d_0 is the minimum particle diameter at which all atoms locate on the surface, usually $d_0 = 6d_a$ for particles (d_a is atomic diameter).

Insert Figure 4.

Fig. 4. Melting point of tungsten decreases with decreasing particle size, especially if <20 nm.

Because the sintering temperature is proportional to the melting point, the sintering temperature of nano-sized particles is thus decreased, as the melting point decreases with the particle size.

The dependence of sintering temperature on particle size is also often described by the scaling law [20-22] as shown in Eq. (3)

$$nln\left(\frac{d_1}{d_2}\right) = \frac{Q}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{3}$$

where d_1 and d_2 are particle sizes, T_1 and T_2 are corresponding sintering temperatures, Q is the activation energy for sintering, and n is a constant depending on sintering mechanisms. For tungsten, it has been shown that n=1/3 for grain boundary diffusion controlled sintering, and Q/R = 4407K [23, 24].

Figure 5 illustrates how the sintering temperature depends on the particle size of W, based on Eq. (3). The two data points are from nano-sized W, with initial particle sizes being 50 and 30 nanometers [15]. The sintering temperatures were determined by the temperature at which over 95% relative density could be achieved by holding for less than 1 hour. Figure 5 demonstrates that the scaling law is valid for the sintering of nano-sized W.

Inert Figure 5

Fig. 5. Dependence of sintering temperature of the milled tungsten powder on particle size described by the scaling law.

Based on Eq. (1)-(3) and Figures 4-5, it is clear that the sintering temperature of nano-sized particles can be explained based on the size dependency on the driving force of sintering. It can be predicted based on the scaling law and/or the melting point of the material as a function of the particle size in the nano-scale range. It should be noted that although the dependence of the sintering temperature on particle size fits the conventional theories of sintering, the significant drop of the temperature required for nano-sized particles to reach densification has important practical implications and significant impact on the industry that produces products based on sintering.

Another significant characteristic of nano-sintering concerns the kinetics of sintering. A theoretical model of the kinetic behavior of nano-sized particles during sintering was put forward by Pan et al., based on a non-linear diffusion theory that is dictated by the large driving force of sintering [25]. Pan showed that the diffusion flux as a function of the driving force is non-linear when the driving force is large,

$$J = \frac{2D}{a\Omega}\sinh\left(\frac{aF}{2kT}\right) \quad (4)$$

where D is a diffusion constant, a is atomic spacing, Ω is atomic volume, k is the Bolzman constant, T is absolute temperature, and F is the driving force. However, when $F \ll kT$, the term sinh(aF/kT) can be approximated as aF/kT, thus Eq. (4) becomes linear, as shown in Eq. (5):

$$J = \frac{D}{kT\Omega}F \quad (5)$$

Figure 6 shows the predictions of the shrinkage during sintering as a function of time for different particle sizes. The Y axis is neck size-to-radius ratio representing shrinkage, and the X axis is time. The solid line is the prediction from non-linear diffusion law, and the dotted line is the prediction from linear diffusion law. It shows that the neck size-to-radius ratio increased more dramatically for a 5 nm particle than that for the 1 μm particle.

Inert Figure 6

Fig. 6. Predictions of the shrinkage during sintering as a function of time for different particle sizes.

However, there are various diffusion mechanisms that could contribute to the sintering of nano-particles. Surface diffusion is widely and logically believed to be extremely fast in the beginning of the sintering of nano-sized particles. Shi et al. studied the initial stage sintering of $BaTiO_3$ particles, and observed the annihilation of small particles by the large particles, or coarsening, which was attributed to surface diffusion [26]. This is an important observation because it touches on the coarsening, which can be viewed as one mechanism of grain growth during the entire process of sintering. This point will be further elaborated in the next section. Note the classic mechanism of grain growth is mainly attributed to grain boundary migration. The initial coarsening may also affect the densification. The interactions between the initial coarsening and the densification are further discussed in the next section.

4. Grain growth of nano-sized powders

To understand the unique features of grain growth during nano sintering, we recognize that the fundamentals, i.e. the thermodynamic driving force and rules do not change. It is the relative contributions of specific mechanisms of mass transport and the kinetics of such mechanistic steps that may differ from that of conventional materials at a larger size scale. Figure 7 shows the classic relationship between grain size and relative density for sintered nano tungsten powder [17]. Similar to the behavior of micron sized particles, there is a period of slow grain growth when the relative density is lower than 90%, followed by exponential grain growth when the relative density is higher than 90%. The process of grain growth can thus be divided into two main stages: the initial stage and the normal (latter) stage. The majority of the grain growth occurs during the latter stage of sintering when density is greater than 90%. This is because the pores in the latter stage of sintering become closed and isolated, and their effects on pinning the grain boundaries are diminished, compared with the open and inter-connected pore channels present during the initial stage of sintering. Therefore, grain boundary migration is the dominant process mechanism for grain growth in the latter stage of sintering.

In contrast, when the relative density is <90%, grain boundary migration is pinned by the open pore channels in the porous body. However, based on the experimental results presented in Fig. 7, it is clear that significant grain growth occurs despite the lack of grain boundary migration. Or, particle sizes are coarser than they were prior to sintering. So, there must be another mechanisms for grain growth during the initial stage. This process must involve mass transport from smaller particles to larger particles by a mechanism such as surface diffusion, which would predominate until the large-to-small particle size ratio between large and small particles reaches a critical value, where the pinning effects of pores on grain boundary migration would no longer be effective. This process, i.e. the increase of the large-to-small particle size ratio, is referred as "coarsening", which will be further elaborated later in this section. In short, the initial stage of grain growth at <90% density is dominated by coarsening, while the latter stage of grain growth at >90% density is dominated by a grain boundary migration mechanism. Again, the latter stage accounts for the majority of grain growth considering the entire sintering process, while the grain growth by coarsening during the initial stage of sintering is also significant. In fact, grain sizes often coarsen to greater than the nanoscale during the initial stage, taking the material outside of the nanoscale region of interest.

Insert Figure 7

Fig. 7. Grain size vs density trajectory during nonisothermal heating of nano tungsten powder from 1073 K to 1673 K (800 ºC to 1400 ºC) (inset: grain size and density during initial coarsening before reaching 90% relative density) [17].

Latter stage grain growth

The latter stage grain growth can be characterized using the conventional power law of grain growth, as shown in Eq. (6):

$$G^n - G_0^n = Kt \tag{6}$$

where G is grain size; G_0 is initial grain size; t is time, and K is a rate constant that depends on the temperature and the activation energy of the process. The exponent n varies depending on the mechanisms. $n = 2$ for grain boundary controlled; $n = 3$ for lattice diffusion controlled grain growth. Grain boundary migration is driven by grain boundary curvature, and involves atoms jumping across grain boundaries. Needless to say, that during the entire process of sintering and grain growth, this is the dominant step responsible for the majority of grain growth.

In order to control the latter stage of grain growth, while maximizing densification, Chen et al. showed how a two-step sintering thermal profile may be used to minimize the grain boundary migration in the latter stage of sintering, as shown in Fig. 8 [27].

Insert Figure 8

Fig. 8. An example of two-step sintering to inhibit latter grain growth by utilizing the kinetic difference between grain boundary diffusion and grain boundary migration.

The sample was initially heated to T_1, and then cooled to T_2, and held at T_2 for a period of time. The results showed that the increase of grain size was halted by holding the sample at T_2, while the relative density continued to increase. It appears that the latter stage of grain growth was successfully avoided while allowing densification to continue. It was theorized that this is because only grain boundary diffusion is active at T_2, while grain boundary migration is only possible at the higher temperature T_1. By utilizing the kinetic differences between grain boundary diffusion and grain boundary migration, the densification and grain growth processes were decoupled.

It is noted here that similar to Fig. 2, the grain size of the first data point is 4-6 times that of the initial particle or grain size. This suggests that there was substantial grain growth during the heating to the sintering temperature T_1. Even though the exponential stage of grain growth was prevented by the two-step sintering techniques, the initial grain growth when relative density was <90%, during coarsening, was not prevented. In many cases, the extent of the initial stage grain growth is so substantial that the grain size of the material is already larger than the nano scale before reaching the isothermal sintering temperature. Therefore, in order to manufacture bulk nanocrystalline materials, the initial stage of grain growth must be understood and controlled.

Initial grain growth

As discussed earlier, the initial stage of grain growth is distinctly different from that of conventional grain growth by grain boundary migration. Grain boundary migration is not an active mechanism at this stage, because of the pinning of the grain boundaries by the open pore channels in the compacts, which are essentially aggregates of particles at this stage. However, contacts or necks between particles that could serve as conduits for mass transport between the particles, would lead to coarsening. The initial increase of grain size is thus accomplished by coarsening of the particles. Figure 9 shows the evolution of the microstructure of nano tungsten during heating from room temperature to the sintering temperature [17]. It shows a consistent evolution from irregular shaped nano-sized particles to gradually more regularly shaped particle with more well delineated crystallinity. These observations also suggest the coalescence of the particles during this process, as the number of particles decreased, and the size of the particles increased dramatically.

Insert Figure 9

Fig. 9. Evolution of microstructure of nano tungsten during heating to different temperatures: (a) 1073 K (800 ºC), (b) 1173 K (900 ºC), (c) 1223 K (950 ºC), (d) 1273 K (1000 ºC), (e) 1323 K (1050 ºC), and (f) 1373 K (1100 ºC).

Wang et al. analyzed the data of grain size changes during the non-isothermal heating process, using both integral and differential modeling techniques [17]. It was shown that the activation energy for the coarsening of tungsten nano particles during heating is between 186-226kJ/mol, which is consistent with that of surface diffusion of tungsten.

To further understand the transition from initial coarsening to grain growth by grain boundary migration, Kumar et al. conducted phase field simulations of the process on a two-unequal-sized-particles model [28]. Figure 10 is a comprehensive illustration of the multiple mechanistic processes that proceed simultaneously, or overlapping with one another, and can be divided roughly into three processes: neck growth, coarsening, and grain boundary migration. It starts with the neck growth at the beginning of sintering, which is followed by the coarsening process when the neck size stabilizes after a period of time. During the coarsening process, the size ratio between large and small particles increases as a result of mass transport from small particles to large particles. It is clear from Fig. 10 that the coarsening process takes the longest time to complete, and is thus the kinetic controlling step for the overall initial grain growth. Once the large-to-small particle size ratio reaches a critical value, grain boundary migration begins, and the grain boundary migration completes rapidly. The critical large-to-small particle size ratio for grain boundary migration is dependent on the dihedral angle of the material and is expressed by Lange [29] as:

$$R_c = -\frac{1}{cos\emptyset_e} \tag{6}$$

where R_c is the critical large-to-small particle size ratio for boundary migration, $\emptyset_e$ is the dihedral angle between the lattices of two adjoining grains. When the large-to-small particle size ratio is larger than R_c, grain boundary migration becomes energetically favorable.

Insert Figure 10.

Figure 10 Illustration of two-unequal-sized-particles sintering process by phase field simulation.

A necessary condition for the coarsening of the particles in the above model is the difference in size between the two particles. The difference in chemical potential between the two particles is the driving force for mass transport through surface diffusion from the smaller to the larger particle. As described earlier [17], surface diffusion is believed to be the mass transport mechanism for coarsening of nano tungsten particles during the early stage of sintering.

Particle size distribution is also key to explaining the relationship between grain size increases and densification. Kingery, Francois, and Lange established a model that explains the dependence of densification on pore coordination number (N) [29, 30]. The pore coordination number (N) is the number of particles immediately surrounding a pore, as shown in Fig. 11. For each material, there is a critical coordination number N_c, which depends on the dihedral angle of the material. When $N < N_c$, the pore is unstable and it will shrink, while if $N>N_c$, the pore is stable. During sintering densification, some mechanism must be active that reduces the coordination number around a pore, so that the pore will shrink and the densification will proceed. Coarsening is one such mechanism that can reduce the coordination number, allowing sintering and densification to continue. In a powder compact with a wide particle size distribution, the chemical potential between different sized particles will drive the coarsening process in which large particles will grow, and small particles will shrink and disappear. Therefore, the coarsening of particles contributes not only to the increase of average grain size, but also to densification (elimination of pores) of the material. Because the coarsening at the beginning of the sintering process is accomplished by surface diffusion, it is therefore inferred that the surface diffusion can indirectly contribute to densification. Further, the indirect role of surface diffusion in initial densification can also be explained as the result of coarsening induced particle rearrangement at the beginning of nano sintering, which is discussed in the literature [31].

Based on the above discussions, we can further deduce that in order to achieve maximum densification with minimum grain growth during nano sintering, it would be most beneficial to have a narrow particle size distribution to minimize coarsening, and to have high green density in order to minimize the pore coordination number and pore size. These observations provide guidance for the development of optimal nano sintering processes.

Insert Figure 11

Fig. 11. Illustration of pore coordination numbers decreasing as a result of particle coarsening.

5. Final remarks

The term “nano sintering” is used here to refer to the process of making bulk nanocrystalline materials by sintering nano-sized particles. If the objective of sintering is solely to achieve maximum densification, nano particles are readily sintered, owing to the extremely high driving force of sintering at the nanoscale. This fact can be utilized in industrial practices.

However, if the objectives of sintering are to achieve maximum densification, and to also retain nanoscaled grain sizes, i.e. make bulk nanocrystalline materials, then the task is more challenging. Although there have been many attempts at controlling and minimizing grain sizes during the isothermal sintering cycle (i.e. the latter stages of grain growth by grain boundary migration), controlling and minimizing the increases of grain size due to the coarsening of particles in the initial stage of sintering has not been addressed. This early stage grain growth occurs as soon as the material is heated, and is as critical as controlling the latter stages of grain growth for achieving nanoscaled grain sizes in the final material. Practically, temperature is the most important factor, compared to the time of the isothermal hold. Especially during heating to the temperature of sintering, the grain size is a function of the temperature. Ideally the temperature during the entire thermal cycle of sintering should not exceed the temperature at which exponential grain growth takes place. However, there must be other mechanisms for achieving maximum densification when the temperature is minimized.

Additionally, surface diffusion is the mechanism behind the initial coarsening of particles. Coarsening of different sized particles contributes to both the increase of average particle or grain sizes, but also densification by reducing pore coordination number and inducing pores to shrink. Therefore, surface diffusion indirectly contributes to the densification in the initial stage of the sintering of nano-sized particles.

Finally, from a practical perspective, a narrow particle size distribution and high green compact density are beneficial for achieving maximum densification with minimum grain growth.

6. Acknowledgements

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Figure Captions

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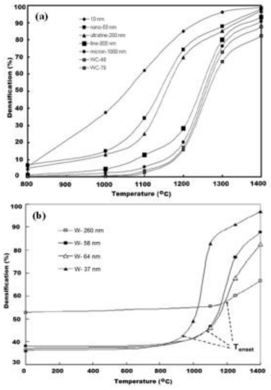
Fig. 7. Grain size vs density trajectory during nonisothermal heating of nano tungsten powder from 1073 K to 1673 K (800 °C to 1400 °C) (inset: grain size and density during initial coarsening before reaching 90% relative density) [17].

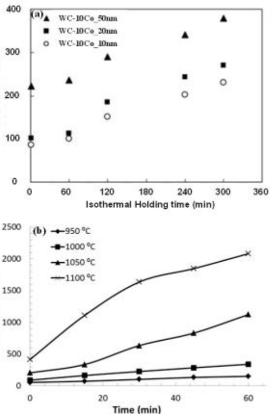
Fig. 8. An example of two-step sintering to inhibit latter grain growth by utilizing the kinetic difference between grain boundary diffusion and grain boundary migration.

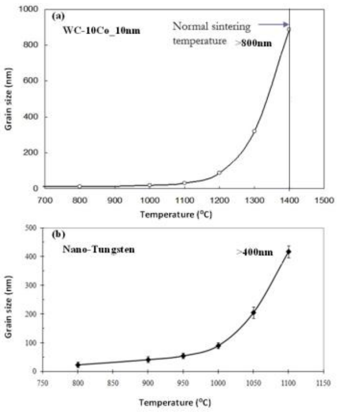
Fig. 9. Evolution of microstructure of nano tungsten during heating to different temperatures: (a) 1073 K (800 °C), (b) 1173 K (900 °C), (c) 1223 K (950 °C), (d) 1273 K (1000 °C), (e) 1323 K (1050 °C), and (f) 1373 K (1100 °C).

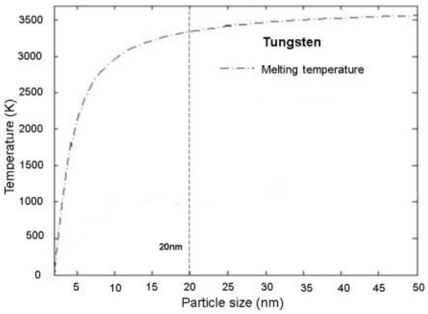
Fig. 10. Illustration of two-unequal-sized-particles sintering process by phase field simulation.

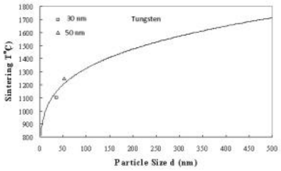
Fig. 11. Illustration of pore coordination numbers decreasing as a result of particle coarsening.

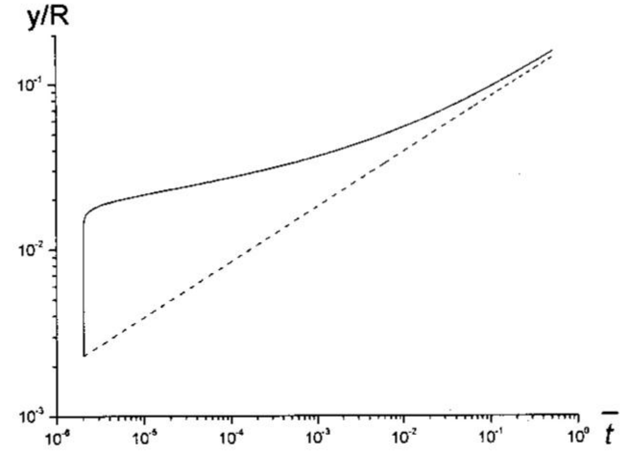
(a)
10 nm
nano-50 nm
ultrafine-200 nm
fine-800 nm
micron-1000 nm
WC-40
WC-75
Densification (%)
Temperature (°C)
0
10
20
30
40
50
60
70
80
90
100
800
900
1000
1100
1200
1300
1400
(b)
W- 260 nm
W- 58 nm
W- 64 nm
W- 37 nm
T_onset
Densification (%)
Temperature (°C)
30
40
50
60
70
80
90
100
0
200
400
600
800
1000
1200
1400


(a)
WC-10Co_50nm
WC-10Co_20nm
WC-10Co_10nm
WC Grain Size (nm)
400
300
200
100
0
0
60
120
180
240
300
360
Isothermal Holding time (min)
(b)
950 °C
1000 °C
1050 °C
1100 °C
Grain Size (nm)
2500
2000
1500
1000
500
0
0
20
40
60
Time (min)

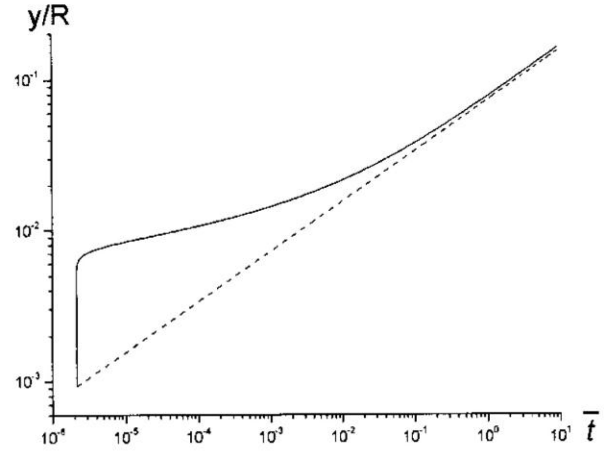

(a)
WC-10Co_10nm
Normal sintering temperature
>800nm
Grain size (nm)
0
200
400
600
800
1000
700
800
900
1000
1100
1200
1300
1400
1500
Temperature (°C)
(b)
Nano-Tungsten
>400nm
Grain size (nm)
0
100
200
300
400
500
750
800
850
900
950
1000
1050
1100
1150
Temperature (°C)


Tungsten
Melting temperature
Temperature (K)
3500
3000
2500
2000
1500
1000
500
0
20nm
5
10
15
20
25
30
35
40
45
50
Particle size (nm)

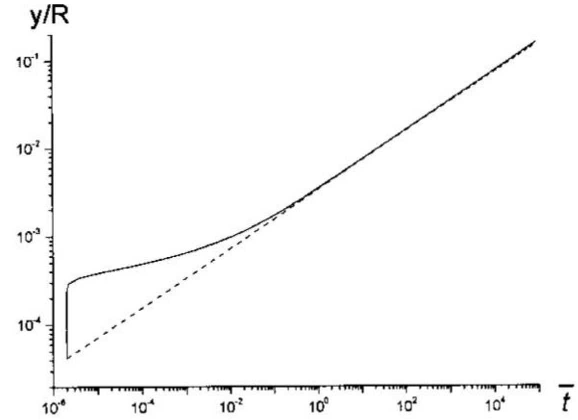

□ 30 nm
△ 50 nm
Tungsten
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
Sintering T°C)
0
50
100
150
200
250
300
350
400
450
500
Particle Size d (nm)



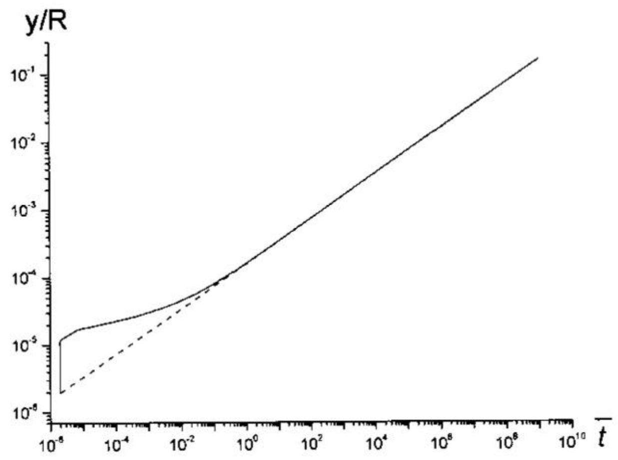
(a) R = 5 nm



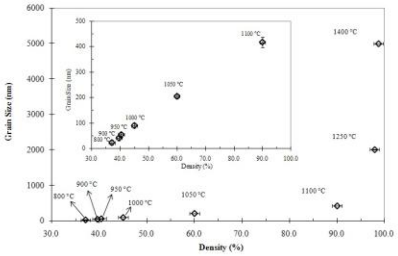
(*b*) R = 10 nm

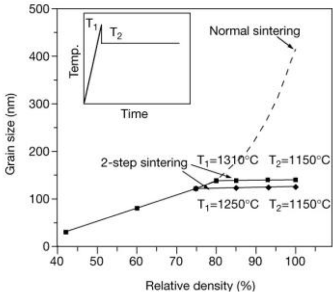


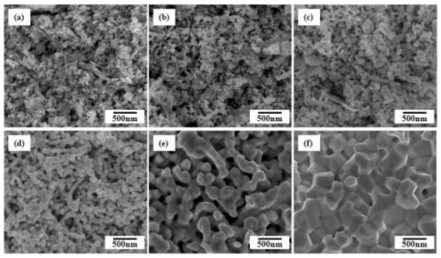
(c) R = 100 nm

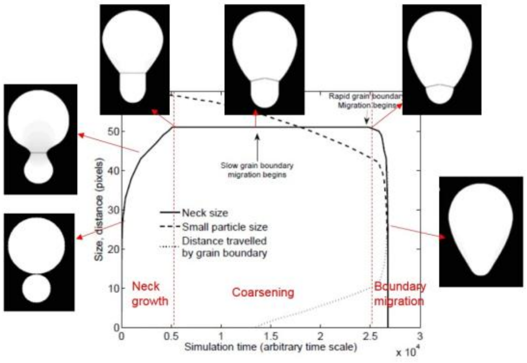

y/R
10⁻¹
10⁻²
10⁻³
10⁻⁴
10⁻⁵
10⁻⁶
10⁻⁶
10⁻⁴
10⁻²
10⁰
10²
10⁴
10⁶
10⁸
10¹⁰
$\overline{t}$

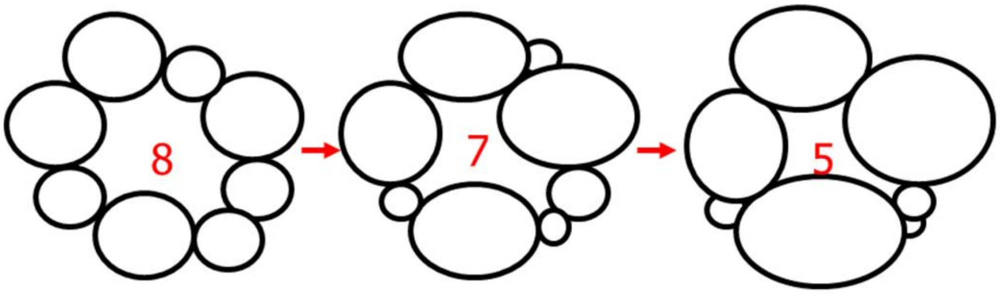
(*d*) R = 1000 nm


6000
5000
4000
3000
2000
1000
0
Grain Size (nm)
30.0
40.0
50.0
60.0
70.0
80.0
90.0
100.0
Density (%)
800 °C
900 °C
950 °C
1000 °C
1050 °C
1100 °C
1250 °C
1400 °C
500
400
300
200
100
0
Grain Size (nm)
30.0
40.0
50.0
60.0
70.0
80.0
90.0
100.0
Density (%)
800 °C
900 °C
950 °C
1000 °C
1050 °C
1100 °C


500
400
300
200
100
0
Grain size (nm)
T1
T2
Temp.
Time
Normal sintering
2-step sintering
T1=1310°C T2=1150°C
T1=1250°C T2=1150°C
40
50
60
70
80
90
100
Relative density (%)


(a)
500nm
(b)
500nm
(c)
500nm
(d)
500nm
(e)
500nm
(f)
500nm


Rapid grain boundary
Migration begins
Slow grain boundary
migration begins
Neck size
Small particle size
Distance travelled
by grain boundary
Neck
growth
Coarsening
Boundary
migration
Size, distance (pixels)
0
10
20
30
40
50
0
0.5
1
1.5
2
2.5
3
Simulation time (arbitrary time scale)
x 10⁴


8
7
5