Modeling the Effect of Particle Packing Density for Sintering

Hanan K. Hassun, Bushra H. Hussein, Bushra. K.H.al-Maiyaly

Physics Department, College of Education for Pure Science (Ibn Al- Haitham)
University of Baghdad, Baghdad, Iraq

E-mail: boshra.h.h@ihcoedu.uobaghdad.edu.iq

Abstract. This research studies the effect of particle packing density on sintering TiO$_2$ microstructure. Sintering experiment was conducted on compacts involving of monodisperse spherical TiO$_2$ particles. The experimental results are modeled using $L^2$- Regression technique in studing the effect of two theoretical values of 55% and 69% of initial packing densities. The mathematical simulation shows that the lower values of density compacts sintered fast to theoretical density and this reflects that particle packing density improved densification rate because of the competing influence of grain growth at higher values of densities.

Keywords: sintering, densification rate, mathematical simulation.

1. Introduction

Synthesis and sintering of nanocrystalline ceramic powders have attracted much attention due to their promising properties [1, 2]. Where sintering is an essential step in the manufacture method of ceramic samples, which can significantly influence the microstructure and properties of materials [3]. The sintering behavior and microstructural development of a powder compact is effect strongly by initial properties, for example the relative density, pore size distribution, the particle and the powder packing. Although the effect of the former parameters on the microstructural development has been examined in detail, the influence of the initial packing values of the powder has been typically over looked [4].

TiO$_2$ is one of the most widely used metal oxides, which has wide range of applications, including gas and humidity sensors, pigments, catalyst support, capacitors and solar cell. TiO$_2$ has been widely studied with respect to synthesis of nano sized powder, thin film fabrication and sintering of nano structured TiO$_2$ ceramics. The properties of nano structured bulk TiO$_2$ ceramic is pretentious by the microstructural topographies for example (grain size, secondary phases, porosity) and defect structure, for example (electronic and point defects) [5, 6].

Effect of particle size distribution on powder packing and sintering in binder jetting additive industrial of metals where a change of bimodal powder mixtures of several particle diameters and mixing parts were printed and sintered to study the influence of bimodal mixtures on the parts density and shrinkage. The using of bimodal powder mixtures develops the flowability (10.5%) and powder's packing density 8.2%, the increasing of the sintered density (4.0%) where reducing of the sintering shrinkage (6.4%) [7].
The intension of this study was modelled mathematically the densification rate of TiO$_2$ powder using L²-Regression modeling technique utilizing two initial packing densities 55% and 69% theoretical.

2. Theoretical part

Sintering is an industrial procedure in which a fine powder that has been formed into a form is subsequently fired at high values of temperatures. The compact when fired densifies and transform non-porous. Sintering is a treatment with thermal that bonds particles composed into a solid, coherent construction, by means of mass transportation apparatuses occurring mostly at the atomic level. Distribution of particle size has an important effect on the sintering procedure and on the microstructure of the sintered part. A wider of particle sizes distribution produced a higher green density and closer sintering in both metals and ceramics [8]. The pores are classified in two basic types: the first type called matrix or first-generation pore and the second type large called second-generation pores which originate from particle agglomeration and particle packing irregularities within the powder compact [9]. The large pores are extra difficult to eliminate large void for two reasons. First simple kinetics dictate along time to fill a larger void by diffusion, second a large pore can be thermodynamically stable depending on the dihedral and pore size: grain size ratio [10].

The densification rate (dp/dt) depends on the diffusion coefficient responsible for densification (D$_{\text{lattice}}$ or D$_{\text{boundary}}$) and the grain size [11].

$$\frac{d\rho}{dt} = \frac{CN_\text{g}DY^\text{G}\Omega}{kTG^L}$$ .................................................(1)

Where C is a constant related to the controlling mechanism, G is the grain size, D is the diffusion coefficient, Y$_\text{c}$ is the gas/solid surface energy, Ω is the material volume, T is the temperature, K is the Boltzmann constant, N$_\text{g}$ is the actual number of pores per grain, L is the grain size exponent, 3 for lattice-diffusion controlled densification which is used in this study [9].

In this study reported in Ref. [13]), the spherical, monodisperse TiO$_2$ powder was created by the hydrolysis of dilute ethanolic solution of titanium tetraethoxide. The powder was discrete in H$_2$O at a pH =8 utilizing probe of ultrasonic, the dispersion was poured into polypropylene vial and the powder was allowable to settle to form concentrated sediments, these diments were collapsed into rigid compacts by the addingsolution of a 1 M (NH$_4$)$_2$CO$_3$ to the clear supernatant in the ampoules. The liquid was extracted and the sediment was gradually dried by air for one day, followed by drying by vacuum at 100 °C for 18 h. the density of particles 3.1 g/cm$^3$ in the compacts was changed to rutile 4.25 g/cm$^3$ by prefiring the contracts at 780 °C for 3 h. It was formed two types of TiO$_2$ compacts, with theoretical density of initial packing of 55 % and 69 %. Samples were heated in air rt of 55°C/ min to the sintering temperatures 1060 °C. The 55% dens compacts were fired at 1060 °C for times reaching from 0.05h to 8.4h. The high value of density compacts was fired at 1060 °C for times ranging from 0.017 to 1h.

The densification rate equation (1) can be written as follows [10];

$$\frac{d\rho}{dt} = \frac{C_3D}{kTG^L}$$ ...............................................................(2)

Where C$_3$ is a constant. The equation (2) can be written as follows:
\[
\frac{d\rho}{dt} = \frac{C_\rho}{TG^L}
\]  

(3)

Where \( C_\rho \) is the densification rate coefficient related to the working mechanisms.

### 3. Regression modeling technique

The equation of \( L^2 \) regression which used in this study can be express as follows [13]:

\[
X = (A^T A)^{-1} A^T b
\]

(4)

Where \( A \) is the matrix , \( A^T \) is the transpose of matrix \( A \) , \( b \) is random observation and \( X \) the fixed part of equation but unknown.

The equation (3) can be written in integral forms as follows:

\[
\rho - \rho_0 = \frac{C_\rho}{T(1-L)} G^{1-L}(t-t_0)
\]

(5)

Equation (5) can be written to another form to make easier to handle with \( L^2 \) regression formulation as follows :

\[
\rho = K_1 G^{1-L} t + h_1
\]

(6)

where \( h_1 \) is the densification rate parameters, \( K_1 \) is the densification rate coefficient

\[
K_1 = \frac{C_\rho}{T(1-L)} h_1 = \rho_0 - K_1 G^{1-L} t_0
\]

The density value was measured using model of \( L^2 \) Regression [14].

### 4. Results and Discussion

The behavior of sintering for the compacts have low -density and high -density compacts are displayed in Fig. 1 and Fig. 2, respectively. Fig. 1 displays the density results as a function of time at 1060 °C. As can be seen from the figure, the less densely packed compact staking the low green density required more time to reach theoretical density ( \( \rho_{th} = 4.25 \text{ g/cm}^3 \) ) than can be seen in Fig. 2. The calculated sintered for low densely sample ranged between 56.37 and 95.64 % , at time 300 min reach 95.64 % for theoretical density. This shows that little grain growth occurred during sintering because of the large mean pore size and corresponding lower green density , where the large pores eliminated at greatlyslower rate caused the decreasing of measured in rate of densification[ 8,11 ].
Figure 1. The density data for 55% of theoretical density as a function of time at 1060 °C.

The calculated sintered for high-density sample in Fig. 2 ranged between 69.12% and 98.57% at time of 19.5 min. The increasing in packing density has resulted in an important increase in kinetics of densification. As can be seen in Fig. 2 to reach 94% for theoretical density needs 10 min only and this has been refer to boundary of grain porosity controller of grain growth kinetics where the competing effect of grains growth occur at high density and the small pores in the green compacts were fast removed. Sample with higher green density had a smaller mean pore size and a thinner distribution of pore size [8, 11].

Figure 2. The density data for 69% of theoretical density as a function of time at 1060 °C.
Fig. 3 shows the comparison for the sintering results for 55% and 69% of theoretical density as a function of time at 1060 °C. As can be seen, the slower rate for low densely sample (55 %) and rapidly rate for high densely sample (69 %), the sign from this that increasing the green density concurrently increases the number of pores per grains and narrow the distribution of pore size and that effect on the densification kinetics that coincide with [15].

![Graph showing density data for 55% and 69% of theoretical density as a function of time at 1060 °C.](image)

**Figure 3.** The density data for 55% and 69% of theoretical density as a function of time at 1060 °C.

In Table 1, we can see the densification rate coefficient $K_1$ and the densification rate parameter $h_1$, both $K_1$ and $h_1$ for high green density (69 %) increases than low green density(55 %) because of effect of the initial partial packing and number of pores on the rate of grains growth and distribution rate.

**Table 1.** Densification rate coefficient $K_1$ and Desification rate parameter $h_1$ for 55% and 69% of theoretical density.

| Densification rate | 55% of theoretical density | 69% of theoretical density |
|--------------------|-----------------------------|-----------------------------|
| Densification rate coefficient $K_1$ | 61.451 | 80.895 |
| Desification rate parameter $h_1$ | 0.926 | 2.0393 |

5. Conclusion

The modeling technique show that the calculated results using $L^2$ Regression technique agrees with experimental results, and the samples that have more densely packed and the higher green density will sintered more quickly than the samples that less densely packed, the density of partical packing and
Porosity uniformity were controlled of the distribution procedures. Therefore, the powder features, especially the green density control the final microstructure and the sintering kinetics.

References

[1] Swihart M T 2003 Current Opinion in Colloid and Interface Science 8 127.
[2] Srdic V V Winterer M and Hahn H 2000 J. Am. Ceram. Soc. 83 1853.
[3] Wang Q B Wang Q G and WanCX 2010 Science of Sintering 42 337.
[4] Björk R Tikare V Frandsen H L and Pryds N 2012 US Department of Energy Publications Paper 105.
[5] Sheng C Vladimir P and Fatih D 2010 Journal of Materials Science 45 (24) 6685.
[6] Ramla MAini S N and Djukan 2019 IOP Conf. Series: Journal of Physics: Conf. Series 1282.
[7] Bai Y Wagner G Christopher B Williams 2017 Journal of Manufacturing Science and Engineering 139.
[8] Alice C DB 2002 Computer modeling of sintering in ceramics University of Pittsburgh.
[9] Zhao J and Harmer MP 1988 J. Am. Ceram. Soc. 71 (2) 113.
[10] Zhao J and Harmer MP 1988 J. Am. Ceram. Soc. 71 (7) 39.
[11] Zhao J and Harmer MP 1992 J. Amer. Ceram. Soc. 75 830.
[12] Barringer E A and Bowen H K 1988 Applied Physics A: Materials Science & Processing 45 (4) 271.
[13] Robert IV b 2001 Linear programming Foundations and extensions seconded Copy right C.
[14] Malyaly HK 2005 Analysis the three stage of sintering using linear programming M.Sc. Thesis University of Baghdad.
[15] Saad B H Farid Sawsan A H Mahdi and Hanan K H Al.Mayaly 2013 Ibn Al-Haitham Jour. for Pure & Appl. Sci. 26 (3).