Software for densification calculation in liquid phase sintering of flat cylinders

10.56238/homeinternationalanais-103

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ABSTRACT

Sintering is an ever-growing area, which requires qualitative and quantitative analysis of the results that justify its effectiveness. This is explained because the results can fundament the decision-making process in sintering. Therefore, in this paper, a coded computer program is introduced to outline and speed up the analysis of the sintering process. This software was designed in Microsoft Visual Basic 6.0®, which enables it to be installed on any Windows®-based device. If adequate values of input data are typed in and operating instructions are followed, the software can provide the following output data related to a flat cylinder: (a) initial density; (b) final density; (c) specific area variation; (d) shrinkage; and (e) densification. The developed software contributes to accelerating and standardizing the analysis of the sintering process, also serving as a baseline for future improvements.

Keywords: Sintering, Densification, Software, Liquid phase sintering.

1 INTRODUCTION

The compacted powder is kept together mainly by adhesive forces, which magnitudes are smaller than those found when the green is sintered. The sintering process promotes bonding inside the crystal lattice. When the geometrical parameters involved allows the development of considerably large contact areas between the particles, green strength may reach high magnitudes. In terms of strength, the bonding established between atoms or ions is of the same order of magnitude as that of a regular lattice. Specifically for multicomponent alloys, although a liquid phase may exist, the solid solution itself has to assure a certain geometrical stability. During this process, fine powders tend to shrink, thus provoking densification. In the case of coarse powders, it is expected adequate dimensional stability.

Consequently, sintering can be defined as a thermally activated material transport in a powder mass or a porous compact, implying a decrease in the specific surface by growing the contacts between the particles, and shrinkage of void volumes (associated with the change of the pore geometry). Therefore, sintering is a heat treatment of a porous compact or a powder mass aiming at improving their desired properties. The process is often accompanied by chemical reactions and fluid-solid interaction. One of the key aspects of sintering is the shift from adhesive contacts or simply pure touching to solid-state bondings (at least two particles share surface atoms) (THÜMMLER, F. and OBERACKER, R., 1993).

As sintering process is composed of the three already described stages, being the former referred to a localized bonding (when there is neck formation), and the latter corresponding to the rounding and shrinkage of the pores (see Fig. 24). The governing quantity of this process is the free surface energy of the particle agglomerate. In the bonding process, there is the transportation of material from the particle nucleus through its thickness until it reaches areas of contact with other particles. Rounding and shrinkage of existing pores demand mass flow from the densest volume to the pore surface, in addition to from softer to sharper corners of the pore surface. The preponderant mechanism of sintering is volume diffusion (HÖGÄNAS, 2013).

In what concerns temperature, it partially consists of heating of the already compacted powder mass at temperatures commonly in the range of 50 to 75% of the melting temperature of the material (if it is a pure component) or that of the lowest melting point constituent (if it is multi-component). This temperature magnitude is held for a controlled and planned time, resulting in particle bonding, which implies an increase in density, hardness, and mechanical strength (CHIAVERINI, V., 1992).

The decrease in system free energy is the leading macro phenomenon of the process, which results from the following circumstances: (a) reduction of specific surface area; (b) decrease in pore volume; (c) elimination of non-equilibrium lattice defect concentrations, and (d) non-equilibrium states (for multicomponent alloys). In this context, if the objective is to design products with high hardness and strength, small particles with similar grain sizes and high density are needed.

Sintering is divided into three stages (THÜMMLER, F. and OBERACKER, R., 1993):

> (a) The contacts between the particles are turned into sintered bridges (necks). Before sintering, micro planes are in contact. As soon as the process takes place, these contact planes are transformed into points of bonding.
> (b) After a certain evolution of neck growth, each particle starts to lose its identity. A new microstructure is then formed.
> (c) At high values of the theoretical density, most of the pore spaces are closed. The remaining pores become sphere-like. When gases are trapped, additional densification becomes impossible (if the gases are indivisible in the solid matrix).

In other words, at the beginning of the process, the material is transported by a diffusional process, influenced by the presence of crystalline defects at the lattice. The diffusional flow promotes the increase in the contact of the particles, verifying an initial bonding between them. The compact starts to present cohesion between particles, however without presenting significant dimensional changes. The higher the green density, the more efficient bonding is (mainly due to the higher contact area). Because of this initial bonding, a neck (which is commonly modeled based on the geometry of two connected spheres with a small volume enclosed by a hyperboloidal surface tangent to the outer surface of the spheres) is then formed. A radius is formed at the ends of the neck (where a grain boundary arises between the two particles). The difference of curvatures between the section corresponding to the radius and the adjacent plane section implies a gradient of vacancies concentration between the neck surface of high curvature (which presents high vacancies concentration) and the adjacent plane surface (which has low vacancies concentration). Because of this, two types of diffusional flows may occur surface and volume diffusion, which are responsible for rounding and spheroidization of irregular powders in a compact. When the atoms flow from the grain boundary to the neck, the vacancies flow in the opposite direction and are thus eliminated at the grain boundary. This causes the approximation between the centers of the two particles, resulting in contraction.

The sintering of a multicomponent alloy may occur with or without a liquid phase. The process also may take place with or without the solid solubility of the components. In the solid state, the potential to be sintered is affected by the responsive stresses, which result from (a) phase inhomogeneities in the mixture;

(b) short-range density range, caused by the compaction; (c) long-range density range, caused by agglomerates; (d) thermal expansion anisotropy (non-cubic phases); (e) thermal expansion mismatch between the existing phases.

The sintering in the presence of a liquid phase is commonly performed aiming at maximizing the density, thus lowering the porosity. There are three stages in this type of sintering (CHIAVERINI, V., 1992):

(a) rearranging: large particle movement in the liquid phase, which promotes the rearrangement of the particles and densification; (b) dissolution and precipitation: occurs only if the solid is soluble in the liquid;

(c) coalescence: in the regions where there are no liquid phases a fast growth of solid grains may occur.

The factors influencing the process are: (a) particle size, in which its reduction promotes more effective sintering; (b) particle composition: impurities restrict the material transportation contrasting with disperse phases in the matrix, which hampers the dislocation movements; (c) particle shape: if the shape favors the contact between the particles, the material transport has more interfaces to interact; (d) green density: an increase in the value of this parameter implies in a denser compacted; (e) time: the sintering degree depends on time mainly in the beginning of the process; (f) particle structure: a fine internal structure and crystalline imperfections imply in more effective sintering due to facilitating diffusional process; (g) temperature: the temperature increase implies in a higher velocity in the process.

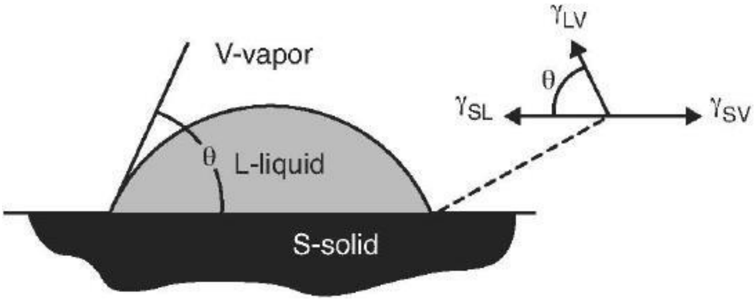
The atmospheres involved in sintering are planned to control the chemical reactions, eliminate impurities, provide convectional heat transfer, eliminate admixtures, impede evaporation of the elements, etc. This is even more relevant when dealing with mixes of powders because two main events simultaneously occur: the alloying and the bonding process itself. The relative proportions of the involved components control the nature of the atmosphere, e.g. if it is decarburizing, carburizing, neutral, oxidizing, or reducing.

The other mean of stress generation is the wetting liquids, which forces the agglomeration of some regions of the powder because of the considerable capillary stresses produced by the liquids. This is modeled using the wetting angle, which is formed at the intersection of vapor, liquid, and solid gases. Also known as contact angle, □, is characterized by the horizontal equilibrium of surface energies (see Fig. 1). Procedurally, □ is measured perpendicularly to the gravity vector. The resulting horizontal solution addresses Eq. (1):

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV}\cos(\theta), \tag{1}$$

where indices SV, SL, and LV correspond to solid-vapor, solid-liquid, and liquid-vapor surface energies, respectively.

Figure 1: A droplet standing on a surface presenting a pictorial definition of the contact angle.

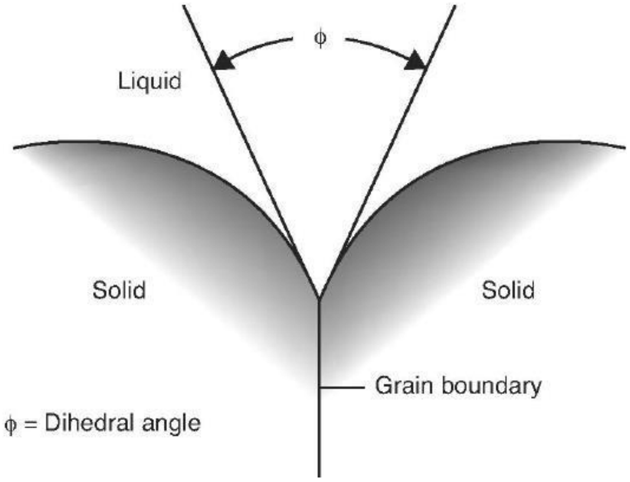


Source: FANG, Z. Z., 2010.

A thermodynamic balance, the so-called dihedral angle, ϕ, is formed by a grain boundary where it intersects with another solid, pore, or liquid during sintering (see Fig. 2). Eq. (2) presents the interrelation with solid-solid and solid-liquid surface energies, γ_{SS}, and γ_{SL}:

$$\varphi = 2\arccos\left(\frac{\gamma_{SS}}{2\gamma_{SL}}\right) \tag{2}$$

Figure 1: Two solid particles interfacing to form the dihedral angle.



Source: FANG, Z. Z., 2010.

In liquid phase sintering, an important non-equilibrium transient is formed when the liquid spreads and penetrates the solid interfaces (if it has enough solubility). The resulting amount of swelling is dictated by the liquid flow into the surrounding pores. The depth of liquid penetration, X, is estimated as a function of the hold time t via Eq. (3):

$$X = \left(\frac{d_P \gamma_{LV} t \cos(\theta)}{4\eta} \right)^{\frac{1}{2}}, \qquad (3)$$

in which η is the liquid viscosity, γ_{LV} is the liquid-vapor surface energy, and d_p is the pore size.

The surface stress corresponds to a non-equilibrium vacancy concentration. Thus, as a function of the curvature, Eq. (4) governs the vacancy concentration under a curved surface:

$$C = C_0 \left[1 - \frac{\gamma \Omega}{K T} \left(\frac{1}{R_1} + \frac{1}{R_2} \right) \right], \qquad (4)$$

in which C_0 is the vacancy concentration corresponding to a flat surface at the same absolute temperature T (equilibrium), Ω is the atomic volume, K represents Boltzmann's constant, and γ is the surface energy (solid-vapor or solid-liquid). Therefore, if the atomic flow is directed from convex to concave surfaces, then the atoms go from regions of vacancy deficiency to regions of vacancy excess. However, atomic motion by volume diffusion requires not only vacancy formation, but also enough energy to break the atom bonding, to release it to the vacant site. The relative number of active atoms N_A is obtained via Arrhenius equation by comparison with the total number of atoms N_0 (Eq. (5)):

$$N_A = N_0 \exp\left(-\frac{Q_B + Q_N}{R T} \right), \qquad (5)$$

where Q_B and Q_N are the energies needed to break the bonds, and responsible for vacancy formation, respectively. Thus, $Q_B + Q_N$ is termed activation energy.

Microstructure Gradients and their Connection to Sintering Thermodynamics

A pore contributes to the surface energy because of the solid-vapor surface energy. As sintering tends to minimize this energy, this implies a reduction in grain boundary energy (through an increase in grain size). If the pore is located at the grain boundary, the energy configuration is low. Otherwise, the product obtained is porous because it is not functional to shrink a pore removed from a grain boundary.

During the intermediate stage, the pores usually form a tubular network attached to the grain boundaries. Going through densification, the pores shrink simultaneously to the grain growth, which stretches the pores in the form of cylinders. As the densification continues, these pores turn into closed spherical pores. The limit condition for this to occur is based on minimization of energy, in which L is the cylindrical pore length (Eq. (6)):

$$L \geq d_P \, \pi. \qquad (6)$$

When high densities are achieved by sintering in the final stage, a relation between the fractional porosity ε_1, pore size, and grain size can be established in the following manner (Eq. (7)):

$$G = \frac{k_1}{R_1 \varepsilon_1} d_P, \qquad (7)$$

in which k1 is a geometric constant, and R1 is the ratio of attached pores to randomly placed pores. There is also a relationship between G and solid-vapor surface area per unit volume, SV, which is associated with the squared porosity (Eq. (8)). This means that if porosity decreases, the pore surface area also decreases, increasing the grain size.

$$G = \frac{1}{S_V} \approx \frac{1}{\varepsilon_1^2}. \qquad (8)$$

A dimensionless parameter, the specific area variation, ks, expressed by Eq. (9), usually represents how the surface area quantitatively behaves related to the initial surface area, Si , where ΔS is the change in surface area.

$$k_S(\%) = \frac{\Delta S}{S_i} 100. \qquad (9)$$

The shrinkage phenomenon can be mathematically defined in a similar way as that introduced by the spring back effect, in the section dedicated to the mathematical modeling of powder metallurgy. Thus, shrinkage, Sk , is defined as the change in length ΔH divided by the initial length Hi (Eq. 10).

$$S_k(\%) = \frac{\Delta H}{H_i} 100. \qquad (10)$$

This phenomenon causes the densification from the green initial density, □i , to the sintered final density, ρ_f, obeying the following expression (Eq. (11)):

$$\rho_f = \frac{m_f}{V_f}, \tag{11}$$

where ρ_i is obtained by the ratio of the green mass mi and the green volume Vi (see Eq. 12).

$$\rho_i = \frac{m_i}{V_i}. \tag{12}$$

Densification can also be defined in terms of these densities (Eq. (13)):

$$\Psi(\%) = \frac{\rho_f - \rho_i}{\rho_i} 100. \tag{13}$$

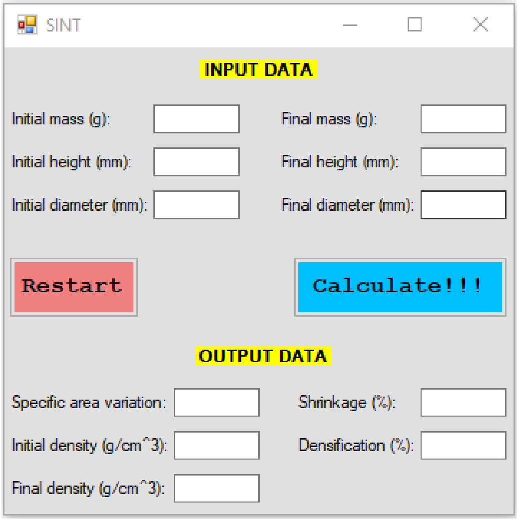
2 METHODOLOGY

This section describes the software developed and the problem to be solved using it.

The software denominated "SINT" was developed in Microsoft Visual Studio 10.0® by emulating the ambient of Microsoft Visual Basic 6.0®. There are six input data: (a) mi , represented by the field "Initial mass (g):"; (b) Hi , corresponding to the field "Initial height (mm):"; (c) Di , associated to the field "Initial diameter (mm):"; (d) mf , represented by the field "Final mass (g):"; (e) H f , corresponding to the field "Final height (mm):"; (f) Df , associated to the field "Final diameter (mm):".

The software aims at providing a tool to calculate the following five output data: (a) ks, represented by the field "Specific area variation:"; (b) H_i , corresponding to the field "Initial density (g / cm3):"; (c) D_i, corresponding to the field "Final density (g / cm3):"; (d) S , represented by the field "Shrinkage:"; and K (e) □ , corresponding to the field "Densification:" (see Fig. 3).

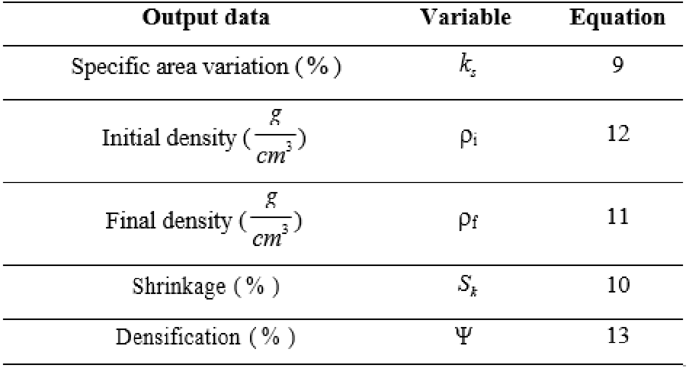
Figure 3: Empty interface of "SINT" software.



Source: own authorship (2022).

There are five output data fields in “SINT” interface. In Table 1, they are associated to the corresponding variable (after the description of the field) adopted in this paper and the referred main equation.

Table 1: Output data in “SINT”, corresponding data, and equations.



Output data	Variable	Equation
Specific area variation (%)	k_s	9
Initial density ($\frac{g}{cm^3}$)	ρ_i	12
Final density ($\frac{g}{cm^3}$)	ρ_f	11
Shrinkage (%)	S_k	10
Densification (%)	Ψ	13

Source: own authorship (2022).

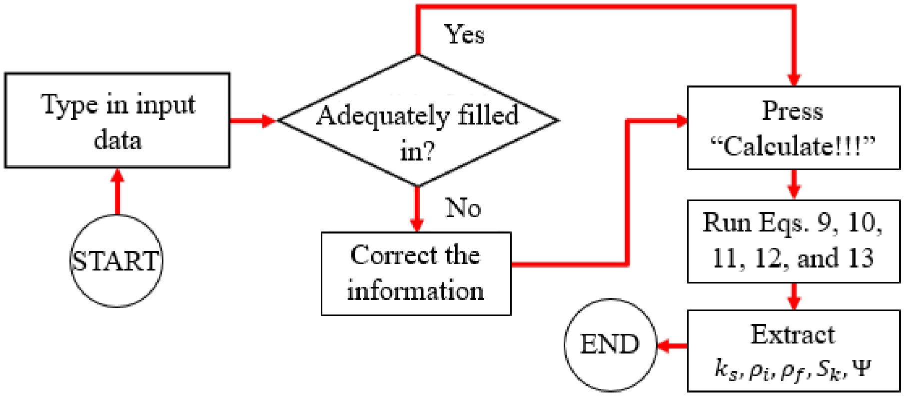
It is important to note that, because of the most diverse branches of uncertainty inherent to the measurement process to input the required data, eventual mistakes may come from the results output by the software. Therefore, it is not possible to guarantee that the real situation will reflect what is calculated by the computer program.

The process of opening the “SINT” software pops up the window shown in Fig. 3. Before filling in, all the fields are in blank state. Six fields have to be filled in as a minimum requirement for calculation. Otherwise, the program will show an error message. After this requirement is fullfiled, the blue “Calculate!!!” button should be pressed, which will result in the five output data filled in by the internal calculation processes. If a new round of calculation have to be performed, the red “Restart” button should be pressed. The software restarts with all the fields in the blank condition.

Regarding its internal architecture, programing sentences adequately disposed are related to each text box, and button. This is done in order to give the referred output data.

Complimentarily, a workflow is provided to show the software operation process. Fig. 4 schematically illustrates this process. The flowchart starts by typing in the adequate information into the six input fields. Care must be taken to fill in all the input fields. Otherwise, the program will return an error message. Typo errors will also result in calculation error. If a non-numerical character is put in any field an error message will appear. If any error message appears, the “Restart” button should be pressed in order to proceed. An alternative procedure is to click the button “X” in the program window, which closes the program. To reopen it, it is necessary to click the corresponding icon. However, if the wrong numerical value is inserted into any field the calculation will proceed anyway. Subsequently, the “Calculate!!!” button should be pressed in order to start the calculation process. If all the input data are filled in an adequate manner, the results can now be read and the process for those input data has finished.

Figure 4: Computer program “SINT” workflow.



Source: own authorship (2022).

The problem proposed herein refers to a flat cylinder corresponding to the input data in Table 2.

Table 2: Input data in “SINT”, corresponding variables, and values.

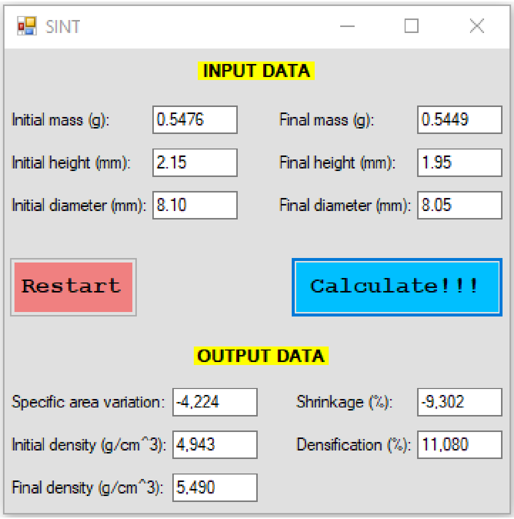
Input data	**Variable**	**Value**
Initial mass (g)	m_i	0.5476
Initial height (mm)	H_i	2.15
Initial diameter (mm)	D_i	8.10
Final mass (g)	m_f	0.5449
Final height (mm)	H_f	1.95
Final diameter (mm)	D_f	8.05

Source: own authorship (2022).

3 RESULTS

The results for the problem just described are presented in Fig. 5. The input data were inserted in the upper part of the interface in accordance with Table 2. The blue “Calculate!!!” button was pressed and the results can be read in the lower part of the program window.

Figure 5: Window of “SINT” with the results for the proposed problem.



INPUT DATA

Initial mass (g): 0.5476
Final mass (g): 0.5449
Initial height (mm): 2.15
Final height (mm): 1.95
Initial diameter (mm): 8.10
Final diameter (mm): 8.05

OUTPUT DATA

Specific area variation: -4,224
Shrinkage (%): -9,302
Initial density (g/cm^3): 4,943
Densification (%): 11,080
Final density (g/cm^3): 5,490

Source: own authorship (2022).

According to Fig. 5, this compacted powder has specific area variation of -4.224%, an initial density of 4.943 g / cm3 , a final density of 5.490 g / cm3 , a shrinkage of -9.302%, and 11.080% of densification.

A negative specific area variation (-4.224%) indicates a little tendency to densification, i.e. a body had a larger surface area before the sintering process and now has a smaller one (presents less porosity). When this information is associated with a negative increment measured in the mass and a positive increment in the cylinder volume after sintering, questions may arise about the densification effectiveness. Corroborating with the mass reduction, the negative calculated shrinkage corresponds to a reduction in cylinder height. The example here calculated is densified in a margin of 11.080%.

Given the results obtained, it may be feasible to use the SINT program to quantify and qualify the sintering process of other materials. The values presented herein can help in the decision-making process about sintering.

4 CONCLUSIONS

This paper introduced the software “SINT” to aid in the sintering process, aiming at quantifying and qualifying the preferred process. It was developed in Microsoft Visual Basic 6.0®, dotted with six input data fields and five output data to be read.

An example of the sintered cylinder was subjected to calculation in this computer program. The entirety of the results obtained converged to the densification of the cylinder.

The developed software is intended to: (a) be a close package encompassing the theoretical background to conduct the sintering process more efficiently; (b) speed up the analysis of sintering; (c) predict the behavior and the results related to the sintered parts; (d) a portable tool, which can be accessed in any Windows®-based device.

ACKNOWLEDGEMENTS

The authors acknowledge the organizers of the event for the opportunity to share this work. They also acknowledge the FAPESP council for funding the research through project 2020/09736-3, CNPq (project 408406/2021-6), and Catalisa/SEBRAE/CNPq (project 29083-128).

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