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PREDICTION OF THE STABILITY MAP OF A NON-CONVENTIONAL SINTERING PROCESS BY USING A DYNAMIC BIFURCATION MODEL

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Abstract. *Flash sintering is an innovative sintering method in which a critical combination of electrical field and temperature triggers a sudden densification within seconds. The conditions for flash sintering should be of a controlled thermal runaway in the voltage control mode that should be changed to current control in order to avoid current localization. Non-linear dynamics can be used to describe this method by the means of a thermal runaway model explaining the evolution of variables during flash sintering. A theoretical processing map for successful flash sintering can be created by using two different transition lines: an explicit solution for the folding points in the voltage control mode temperature equilibrium surface and a criterion for the formation of hotspots based on perturbation methods. The results of this analysis show that the hotspot formation is inherent to the voltage control mode as a function of materials properties, process variables and sample geometry. The stability of the voltage and current control modes is examined by the use of bifurcation theory and can explain the asymptotic behavior in the current control mode in conventional flash sintering and the whole process evolution the method of current ramp controlled flash sintering.*

Keywords: *Bifurcation, Flash Sintering, Processing Map*

1. INTRODUCTION

Flash sintering is a recent method in which sudden densification is reached in seconds when a critical threshold of electrical field and furnace temperature are reached (Cologna *et al.*, 2010). The usual experimental procedure for flash sintering is to apply a constant electrical field (Stage I) to a sample in a furnace, which leads to a non-linear conductivity surge (Stage II) followed by a needed shift to current control (Stage III) to avoid excessive thermal runaway. The phenomenon was already observed for a wide range of ceramics with conductivities ranging over orders of magnitude. The process was shown to be possible with materials with conductivities as low as doped alumina (Cologna *et al.*, 2011) and for semiconductors such as uranium oxide (Raftery *et al.*, 2017). For further information on the process and the developments related to it, extensive reviews were given by Dancer (2016), Yu *et al.* (2016) and Biesuz and Sglavo (2019).

One of the fundamental mechanisms to describe the flash sintering process resides in the fact that the main trigger is a thermal runaway process which depends on the conditions of the experiment. This thermal runaway is caused by the positive feedback generated by the Joule heating being dissipated in the material coupled with the Arrhenius-type dependance of the resistivity of the ceramic materials. Models describing thermal runaway in flash sintering were developed by different authors, with approaches including a finite-difference model (Todd *et al.*, 2015), onset criteria based on approximations of the heat balance in the sample (Dong and Chen, 2015b,a; Dong *et al.*, 2016; Zhang *et al.*, 2015) and a dynamical bifurcation model (da Silva *et al.*, 2016). This work intends to further develop the bifurcation model and discuss the features concerning the modes of voltage and current control.

With the objective of scaling up the flash sintering process, researchers have found out that critical values of voltage and current can lead to the formation of a localized thermal runaway, or hotspots (Trombin and Raj, 2014) that can induce the destruction of the sintering body by inhomogeneous densification. Dong (2017) has presented a simplified mathematical analysis using perturbation theory in order to describe the hotspot formation in flash sintering. However, there are still some open questions regarding the critical values for the formation of hotspots and the existence of those hotspots in the current control mode (Stage III).

This paper deals with a model-based approach to calculate the processing windows for flash sintering. In order to be able to calculate the critical values of current and electrical field to denote the different regions in the processing map, the approach in this paper is divided in two main sections: one developing an explicit analytical solution for the onset temperatures of the thermal runaway model based on the model presented at da Silva *et al.* (2016). Secondly, a calculation of the critical values for the formation of hotspots is shown by using a perturbation method, and its relationship with the current control mode is also discussed.

2. Modeling

2.1 Processing Map Calculation Methodology

The flash sintering behaviour depends strongly on the voltage and current limit chosen to perform the experiment. By exploring those parameters, a processing map can be established (Figure 1) showing three distinct behaviors: no flash, homogeneous flash sintering (Safe region) and current localization (Fail region) (Trombin and Raj, 2014). Two main features are observed: A critical electrical field in which flash is observed regardless of the set current limit, and a critical combination of electrical field and current limit, at which current localization occurs.

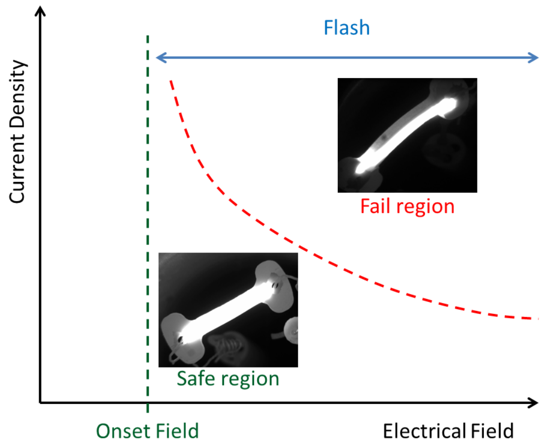

Figure 1. Schematics of a Processing Map

The modeling approach aims to calculate those two critical lines delimiting the processing map. The flash transition is determined by the critical electrical field that causes thermal runaway. The transition between the Safe and Fail regions is determined through the condition of the generation of hotspots. This is done by using the perturbation approach already established in microwave sintering (Hill and Marchant, 1996; Manière *et al.*, 2017).

2.2 Onset of Flash Sintering

The transition from the enhanced sintering observed at moderate electrical fields to flash sintering can be calculated using the thermal runaway model presented in different forms by many researchers (Todd *et al.*, 2015; Dong and Chen, 2015b,a; Dong *et al.*, 2016; Zhang *et al.*, 2015; da Silva *et al.*, 2016). In this paper we choose to follow the procedure described in da Silva *et al.* (2016), and as a further development an explicit relationship to calculate the folding points of the equilibrium surface is presented.

Temperature evolution in the sample during flash sintering in the constant voltage stage can be described by solving the heat equation in a lumped model considering Joule heating and the heat losses to the furnace. For the bifurcation analysis, it is important to calculate the equilibrium points of the sample, hereby denoted when $\frac{d\theta}{dt} = 0$ (da Silva *et al.*, 2016):

$$\rho c_p \frac{d\theta}{dt} = \frac{E^2}{r_0} e^{-\frac{\Delta E}{k\theta}} - L(\theta) = 0 \tag{1}$$

where ρ is the material density, c_p is the specific heat capacity, θ is the sample temperature, E is the applied electrical field, r_0 is the preexponential factor for the resistivity, ΔE the activation energy for resistivity, k is the Boltzmann constant and $L(\theta)$ is a heat loss function denoting convection (L_c) or radiation (L_r), depending on the furnace conditions:

$$L_c(\theta) = h\frac{A_t}{V}(\theta - \theta_0) \tag{2}$$

where h is the convection heat transfer coeffient, A_t is the transversal area of the sample, V is the volume of the sample and θ_0 is the furnace temperature.

$$L_r(\theta) = \sigma\epsilon\frac{A_t}{V}(\theta^4 - \theta_0^4) \tag{3}$$

where σ is the Stefan-Boltzmann constant and ϵ is the material emissivity.

The equilibrium surfaces described by equation (1) in the radiation case (Figure 2) have a special quality in which they 'fold' at critical values of electrical field and furnace temperature. The sudden current surge in flash can be explained as a 'jump' from the lower level of the surface (which starts in $\theta = \theta_0$) to the higher level, in the cases where there are three stable points. If the value of θ_0 is high enough (as can be seen for values greater or equal than 0.2 in the figure), no sudden 'jumps' are observed, and therefore only enhanced sintering occurs.

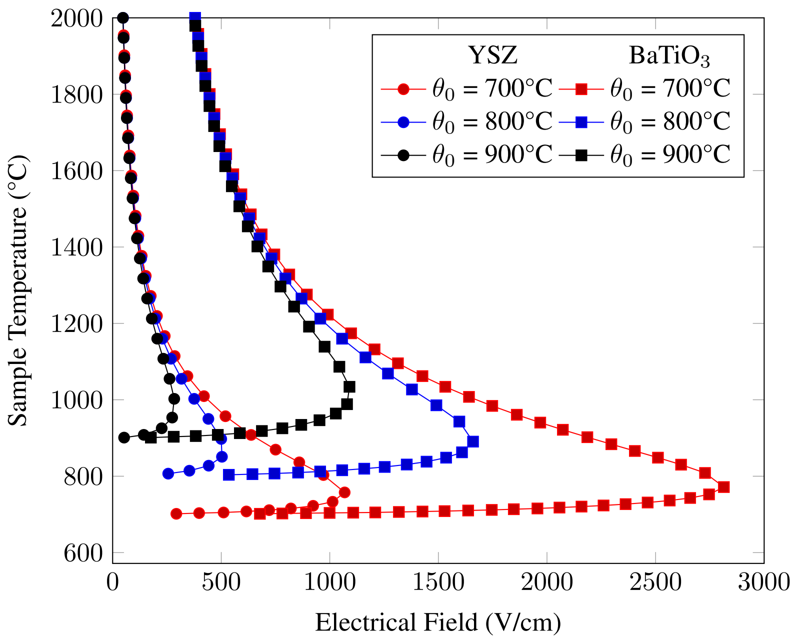

Figure 2. Bifurcation diagram (Equation 1) for the single phases of YSZ and barium titanate. Properties values taken from da Silva *et al.* (2016).

The existence of the critical points, or the folds on the surface of Figure 2, can be calculated via implicit differentiation as a function of temperature of the surface described by equation (1). This procedure is described in detail in the appendix for the radiation and convection cases. By following this procedure, it is possible to obtain an explicit relationship between critical electrical fields and furnace temperatures for the onset of flash sintering in the radiation case:

$$\theta_0 \geq \frac{1}{25} \frac{5^{0.75}\left[\left(4+5W\left(\frac{2^{0.4}}{5\left(-\frac{E^2}{Z_r y^4}\right)^{0.2}}\right)\right)\left[W\left(\frac{2^{0.4}}{5\left(-\frac{E^2}{Z_r y^4}\right)^{0.2}}\right)\right]^3\right]^{0.25} y}{\left[W\left(\frac{2^{0.4}}{5\left(-\frac{E^2}{Z_r y^4}\right)^{0.2}}\right)\right]^2} \tag{4}$$

In this case, the grouping of variables $y = \frac{\Delta E}{k}$ and $Z_r = r_0 \sigma \epsilon \frac{A_t}{V}$ is used for convenience. $W(x)$ denotes the Lambert W function, which is the inverse relationship to the function xe^x.

It is worth noting that the solution itself (Figure 3) will be two-branched because it includes a negative argument on the Lambert W function (Corless *et al.*, 1996; Chatzigeorgiou, 2013), where the solution relating to the $W(-1,x)$ branch shows the critical point flash onset point as exemplified before. The solution related to the $W(0,x)$ has no direct physical meaning, but when both solutions meet, no fold will exist, because the argument of the Lambert W function $\left(\frac{2^{0.4}}{5\left(-\frac{E^2}{Z_r y^4}\right)^{0.2}}\right)$ is smaller than $-\frac{1}{e}$, denoting the areas where only enhanced sintering occurs instead of the surge observed in flash sintering. This critical point also defines the critical furnace temperature in which values higher than $5^{-\frac{5}{4}}y$ suppress the bifurcation, leading to a region where flash is not possible (Figure 3). This is an interesting finding, because it rationalizes the fact that the onset temperature can be changed by the heat transfer conditions, but the critical furnace temperature is a material-only controlled effect, because it does not depend on Z_r.

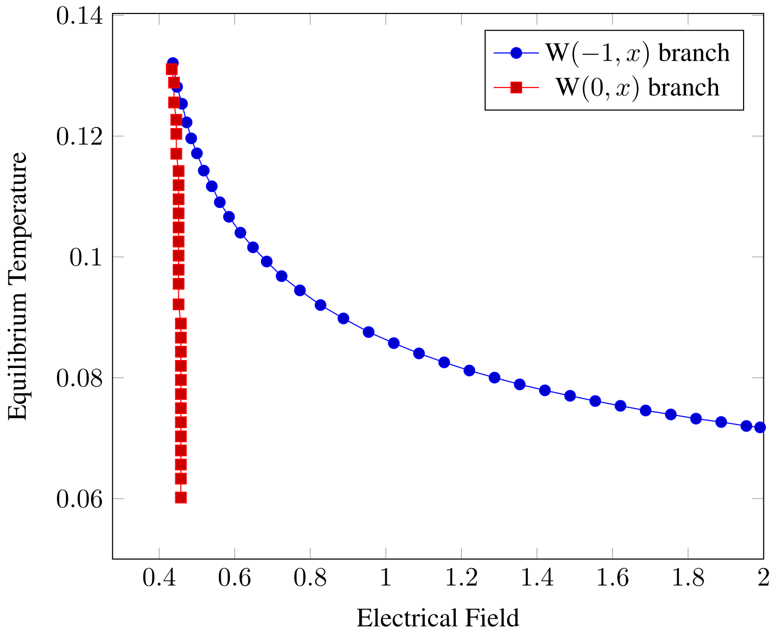

Figure 3. Calculation of the surface folding points for the radiation case (Eq. 4). Blue: W(-1,x) branch; Red: W(0,x) branch.

The same procedure can be repeated for the convection form of the energy balance:

$$\theta_0 \geq -y \frac{1 + 2W\left(-\frac{\sqrt{Z_c y}}{2E}\right)}{4\left[W\left(-\frac{\sqrt{Z_c y}}{2E}\right)\right]^2} \tag{5}$$

In this case, the grouping of variables $y = \frac{\Delta E}{k}$ and $Z_c = r_0 h \frac{A_t}{V}$ is used for convenience.

The solution itself (Figure 4) has the same qualitative behaviour as the radiation one.

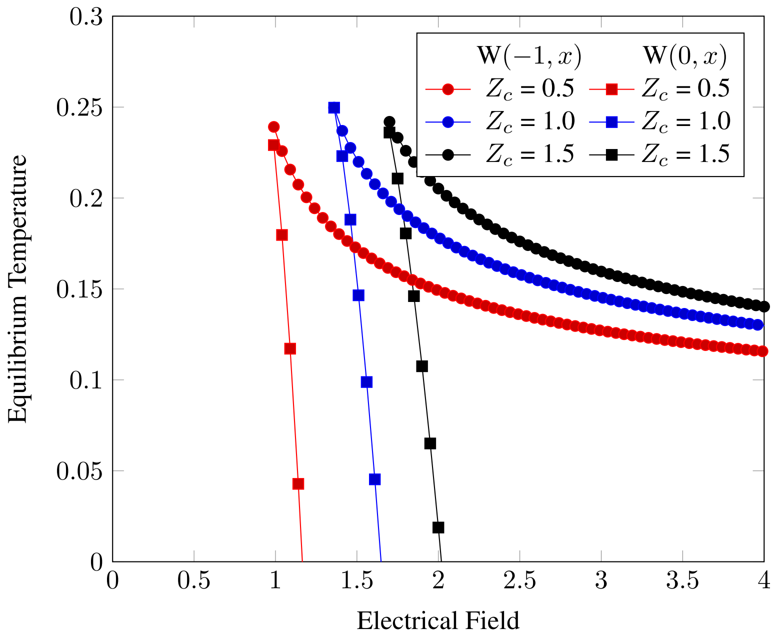

Figure 4. Calculation of the surface folding points for the convection case (Eq. 5) for different Z values.

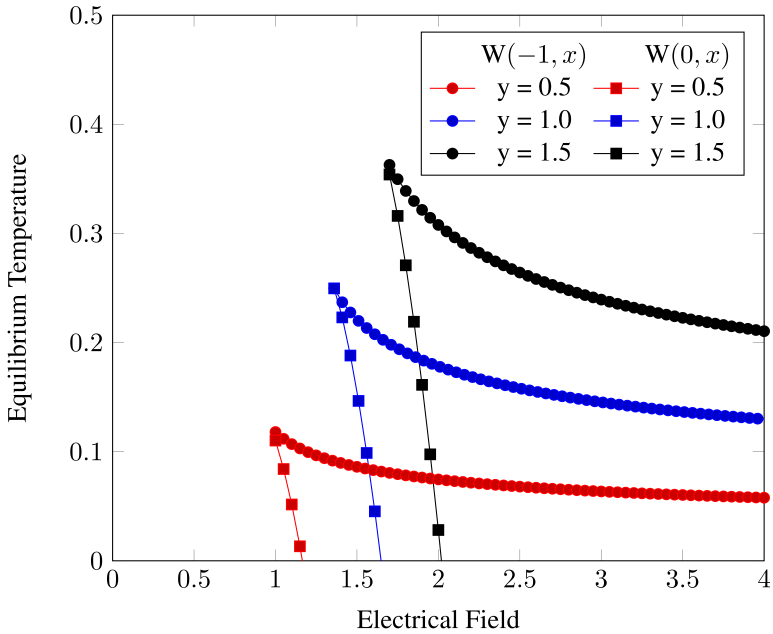

Figure 5. Calculation of the surface folding points for the convection case (Eq. 5) for different y values.

In the convection case, the critical furnace temperature for flash should be lower than $\frac{\Delta E}{4k}$ and the critical electrical field higher than $\frac{e\sqrt{Zy}}{2}$.

2.3 From Safe to Fail: Hotspots in Flash Sintering

In order to understand the critical values for the formation of this current localization, the formation of hotspots can be modeled using the approach for hotspot formation already estabilished in microwave sintering (Hill and Marchant, 1996; Manière *et al.*, 2017) and used for the first time for the voltage control mode in flash sintering by Dong (2017). The formulation is based in the heat equation being applied to the material, taking into account the Joule heating and the internal heat dissipation inside the sample:

$$\rho c_p \frac{d\theta}{dt} = \frac{E^2}{r_0} e^{-\frac{\Delta E}{k\theta}} + \kappa \frac{d^2\theta}{dx^2} \tag{6}$$

To understand how heat would be dissipated along the sample in a uniform manner, one can introduce a small sinusoidal perturbation multiplied by an exponential temporal term and then observe its behaviour as a function of time (Hill and Marchant, 1996; Manière *et al.*, 2017; Dong, 2017):

$$\theta = \theta_0 + \alpha \sin\left(\frac{x}{\lambda}\right) e^{-\beta t} \tag{7}$$

Where α is the amplitude of the sine oscillation, λ is the characteristic thickness of the sample (in the present case, the distance between the center of the sample and the closest surface. For dogbone samples it is half of the smallest thickness in the cross-section, and for cylindrical samples is the radius) and β is the damping term of the oscillation. The idea behind the perturbation method is to analyse the sign of β. If β is positive, the perturbation is damped with time. If negative, any perturbations will grow exponentially.

It is possible to estimate the value of β by approximating the Joule heating term in equation 6 by a Taylor series approximation with respect to the variable x and using equation 8 and reorganizing the terms. The instability criteria can be defined as (Dong, 2017):

$$\beta = \frac{1}{\rho c_p} \left[\frac{2\kappa}{\lambda^2} - \frac{E^2}{r_0} e^{-\frac{\Delta E}{k\theta_0}} \frac{\Delta E}{k\theta_0^2} \right] \tag{8}$$

Therefore, the criteria for the formation of hotspots is the critical characteristic thickness λ. Therefore, hotspots will occur only if (Dong, 2017):

$$\lambda^2 \geq \frac{2\kappa}{\frac{E^2}{r_0} e^{-\frac{\Delta E}{k\theta_0}} \frac{\Delta E}{k\theta_0^2}} \tag{9}$$

Meaning that for λ smaller than the actual characteristic thickness of the sample, the flash only happens locally, leaving parts not densified. It can be seen that the $\frac{E^2}{r_0}e^{-\frac{\Delta E}{k\theta_0}}$ term can be directly related to the power dissipation in the sample, by relating it to Ohm's law. Therefore, the hotspot criteria can be defined as a function of the processing parameters:

$$\lambda^2 \geq \frac{2\kappa}{Ej\frac{\Delta E}{k\theta_0^2}} \tag{10}$$

In order to define the hotspot criterion for the current control mode, it is possible to repeat the same procedure for the current control mode:

$$\rho c_p \frac{d\theta}{dt} = j^2 r_0 e^{\frac{\Delta E}{k\theta}} + \kappa \frac{d^2\theta}{dx^2} \tag{11}$$

The main difference is in the Joule heating term, which in this case has a different form in the exponential behavior. By applying the same procedure, the instability criteria can be defined as:

$$\beta = \frac{1}{\rho c_p}\left[\frac{2\kappa}{\lambda^2} + \frac{E^2}{r_0}e^{\frac{\Delta E}{k\theta_0}}\frac{\Delta E}{k\theta_0^2}\right] \tag{12}$$

Therefore, in the case of current control, β will always be positive and the perturbations will be damped by the system. This means that the hotspots are always formed in the voltage control mode.

With the limits here defined in the previous section, the processing map shown in Figure 1 can be drawn by using the onset criteria defined in equations 4 or 5 and the hotspot formation criterion defined in equation 10. It can be observed in equation 10 that the range of the safe conditions for homogeneous flash sintering are widened at higher furnace temperatures and with samples of smaller size.

3. Conclusions

Using the thermal runaway model and the criteria for the formation of hotspots, theoretical processing maps can be created. They are a guideline in order to find optimal processing parameters of voltage and current limits in order to reach the flash sintering conditions and at the same time, avoid the formation of hotspots.

The thermal runaway model predicts the onset of the flash sintering process. It can provide a quick tool in order to define the electrical field - temperature pair for flash sintering. An explicit relationship between critical electrical field and furnace temperature is shown for both cases of radiation and convection heat losses. This theory can explain important features of flash, including the minimum critical electrical field for flash and the maximum furnace temperature for the presence of the flash process.

By the use of perturbation theory, it was shown in equation 10 that the formation of hotspots is directly proportional to the power dissipated and inversely proportional to the square of the onset temperature in the voltage control mode. The model was tested for a wide range of geometries, compositions, electrical fields and current limits. A further outlook for future work is to test the influence of different heating rates in the shape of the processing map. The same modeling procedure was applied to the current control mode, with the conclusion that no hotspot formation is possible in this mode, since all the perturbations are damped by the system. This should have some large implications in the applicability of flash sintering in larger scales and related processing parameters.

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A Calculation of the Folding Points

A 1 Radiation

From equations (1) and (3):

$$E^2 e^{-\frac{y}{\theta}} - Z(\theta^4 - \theta_0^4) = 0 \tag{13}$$

Implicit differentiation to calculate $\frac{dE}{d\theta}$ leads to:

$$\frac{dE}{d\theta} = \frac{-4Z\theta^5 + E^2 y e^{-\frac{y}{\theta}}}{2E\theta^2 e^{-\frac{y}{\theta}}} \tag{14}$$

To calculate the folding points, it is needed to solve $\frac{dE}{d\theta} = 0$ for θ. The only real root is:

$$\theta = -\frac{y}{5W\left[\frac{1}{5\left(-\frac{E^2}{4Zy^4}\right)^{0.2}}\right]} \tag{15}$$

Replacing θ in A.1 by A.3:

$$E^2 e^{5W\left[\frac{1}{5\left(-\frac{E^2}{4Zy^4}\right)^{0.2}}\right]} + Z\left[\left(\frac{y}{5W\left[\frac{1}{5\left(-\frac{E^2}{4Zy^4}\right)^{0.2}}\right]}\right)^4 + \theta_0^4\right] = 0 \tag{16}$$

Using the Lambert W property $e^{nW(x)} = \left(\frac{x}{W(x)}\right)^n$ and further simplification leads to equation (4).

A 2 Convection

From equations (1) and (2):

$$E^2 e^{-\frac{y}{\theta}} - Z(\theta - \theta_0) = 0 \tag{17}$$

Implicit differentiation to calculate $\frac{dE}{d\theta}$ leads to:

$$\frac{dE}{d\theta} = \frac{E^2 y e^{-\frac{y}{\theta}} - Z\theta^2}{2E\theta^2 e^{-\frac{y}{\theta}}} \tag{18}$$

To calculate the folding points, it is needed to solve $\frac{dE}{d\theta} = 0$ for θ. The only real and positive root is:

$$\theta = -\frac{y}{2W\left(-\frac{\sqrt{Zy}}{2E}\right)} \tag{19}$$

Replacing θ in A.5 by A.7:

$$E^2 e^{2W\left(-\frac{\sqrt{Zy}}{2E}\right)} + Z\left[\frac{y}{2W\left(-\frac{\sqrt{Zy}}{2E}\right)} + \theta_0\right] = 0 \tag{20}$$

Using the Lambert W property $e^{nW(x)} = \left(\frac{x}{W(x)}\right)^n$ and further simplification leads to equation (5).

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