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## On thermal runaway and local reactions during flash sintering of ceramic nanoparticles

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### Highlights

- Free molecular heat transfer imposes temperature gradient at the nanoparticle surfaces.
- Internal and external nanoparticles preserve and lose the radiated heat, respectively.
- Flash event is due to current percolation via the locally softened particle contacts.
- Thermal runaway associated with local particle surface melting and its solidification.

### 1. Introduction

Flash sintering (FS) is a novel technique associated with simultaneous application of electric and thermal fields for ultrafast densification of the ceramic nanoparticle compacts within a few seconds. Different investigators suggested different densification mechanisms for FS mainly due to uncertainty in the actual local temperature measurements. Here, we performed numerical analysis of the heat balance at the flash event assuming simultaneous surface softening/liquid formation and current percolation through the nanoparticle contacts. This paper is in press in J. Mater. Sci. [1].

### 2. Methods

Assuming inter-particle radiations in the specimen volume, the electric Joule heat generated at the nanoparticle contacts partially lost by radiation from the specimen external surfaces. Considering the thermal effects due to rapid heating rate and free molecular heat conduction regime, high temperature gradients between the nanoparticle surfaces and the surrounding gas were developed. The heat balance expressed by:

$$\rho \rho_o c_p \frac{dT}{dt} = \frac{L_s V^2}{A_{cs} R_e} - \rho \cdot \frac{A_s}{V_s} \cdot \varepsilon_{em} \sigma_{SB} (T_{surf}^4 - T_{furn}^4) \quad (1)$$

When liquid forms at the nanoparticle contacts, the change in the internal heat calculated according to the following equation [2]:

$$\dot{Q}_{int} = [\rho_s c_p^{solid} (1 - x_{melt}) + \rho_l c_p^{liquid} x_{melt}] \frac{dT}{dt} \quad (2)$$

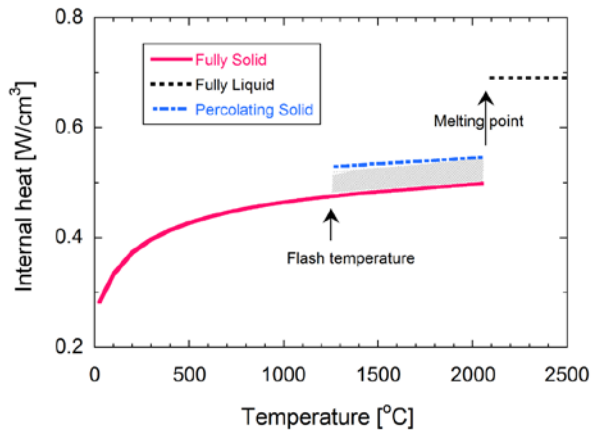
where  $x_{melt}$  is the volume fraction of the melt, and indices  $s$  and  $l$  refer to solid and liquid, respectively. Since current percolation is associated with the percolation phenomenon, the volume fraction of the melt is 0.247 at the invasive percolation threshold [3] and the flash event.

### 3. Results and discussion

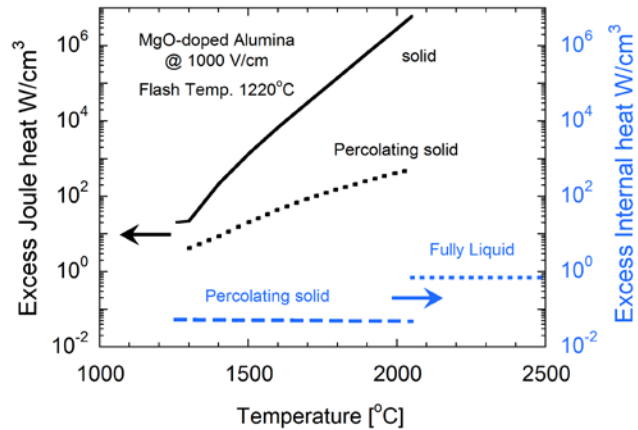
Let us assume heating the specimen from room temperature to above its melting point, without an electric field. It will generate internal heat corresponding to the heat capacity of the specimen mass, as a solid and as a liquid. The internal heats that the alumina specimen [4] can store as a solid bulk, as a partially melted solid (at the percolation threshold), and as fully liquid, were calculated versus temperature, and shown in Figure 1. The internal heat in the solid state (solid red curve in Figure 1) increases with temperature up to the melting point ( $T_m = 2050^\circ\text{C}$ ). At this temperature, melting is associated with an enthalpy of fusion, due to the endothermic nature of the melting. The internal heat of the fully melted specimen also shown (dotted back line) in Figure 1. The internal heat of the partially melted solid at the percolation threshold, i.e. solid with liquid volume fraction of 0.247 (formed only at the flash temperature) also shown (dashed-dotted blue curve) in Figure 2. We calculated the internal heat for this percolating system using the phase assemblage equation (2). The hatched area in Figure 2 represents the excess internal heat between the percolating system and its

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non-percolating solid counterpart. This excess heat represents the heat invested for partial melting as needed in the percolative system. We calculated the excess Joule heat versus temperature, and compared it with the excess internal heat due to the partial melting (percolating solid), as shown in Figure 2.



**Figure 1** Internal heat versus temperature in MgO-doped alumina specimen similar to that in ref. 4 assuming fully solid granular (solid red curve), granular solid with percolation through the liquid (dashed-dotted blue curve) and fully liquid (dotted black line). The hatched area represents the excess internal heat needed to form the percolating liquid at the flash temperature.



**Figure 2** Excess Joule heat generated, and excess internal heat needed to form a liquid, versus temperature, for MgO-doped alumina specimen in ref. 4 at different states. The states include fully solid granular, fully liquid, and granular solid with percolation through the liquid.

As mentioned above, partial melting may take place at the temperature, when the gain in the excess Joule heat surpasses the heat invested for the partial melting. For comparison, the heat needed for full melting of the specimen also shown in Figure 2 (horizontal dotted blue line). It is clear from Figure 2, that already at the flash temperature, the excess Joule heat is higher by one to two orders of magnitude than those needed for partial or full melting of the specimen.

## 4. Conclusions

The excess Joule heat at the flash temperature suffices the excess heat necessary for local contact softening/melting, through which the electric current percolates. Formation of liquid at the contact points increases the overall electric conductivity by two to four orders of magnitudes and enables the rapid densification kinetics by nanoparticle rearrangement and densification aided by the attractive capillary forces of the melt. The transient nature of the local melt leads to its solidification immediate to the nanoparticle rearrangement. Therefore, thermal runaway in flash sintering refers to the local softening/melting at the nanoparticle surfaces and their immediate solidification.

## References

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## Keywords

Flash sintering; Nanoparticles; Modeling; Thermal runaway.