

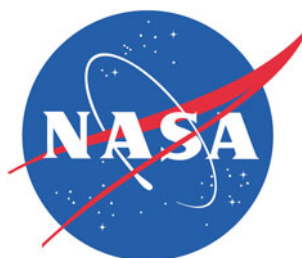
Bill Lee  
Rainer Gadow  
Vojislav Mitic  
*Editors*

# Proceedings of the IV Advanced Ceramics and Applications Conference

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Bill Lee · Rainer Gadow  
Vojislav Mitic  
Editors

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# Foreword

In the phase of a European mandate in the Balkan countries, 5 years ago, I helped promote the idea of jointly launching a ceramic conference in Serbia with academic institutions, universities and the Serbian Ceramics Society. It started off with a moderate agenda focused on the lecturers from Serbian universities and research institutes and some support from local industry and government. This event quickly grew into a ceramics conference of European dimension with top-class speakers from all over Europe and even the USA, Canada, Japan and Iran. It should also be mentioned that this Serbian ceramics conference contains also impressive poster session and exhibitors.

The proceeding of this conference is an excellent blueprint containing papers of high standard and reviewed by an international panel of recognized professors and scientists. It is a welcome step in bringing the ceramics sciences and technologies to the Eastern European countries with the challenges of collaboration between Western and Eastern European scientists and institutes/universities. In addition, it provides an appetizer of breakthroughs and innovations in the Balkan countries.

I find the ambitious approach to cover the whole value chain from basic research, through engineering and technology to applications as well as the implications for societies including environmental aspects, very impressive. This book covers many topics from nanomaterials and nanocomponents, from fundamentals of composition, structure and properties to syntheses and processing aspects, characterization, analytical techniques and modelling. It also concerns the conservation and protection of cultural heritage: conservation and restoration, ceramics application in medicine and human health.

This book motivates education and offers an emerging field of research and innovation. It is a source of information and points to new ideas and lists a large number of recommendations for all those involved in ceramics research and development; finally, it provides a potential for societal and economic benefits, including job creation.

The proceedings are a great initiative and will stimulate ceramics sciences and technologies in Eastern Europe especially in Serbia, with spin-offs for industrial innovations. For this reason, I believe that these proceedings should receive the attention, the involvement and the support wholeheartedly by Eastern European governments, policy-making bodies: International organizations as the World Bank, government agencies, cultural foundations, etc., European Union and countries and regions; foundations, research agencies and industries in upgrading investments and research needs and foster European and worldwide collaboration.

The great efforts put forward by the Serbian government, the Serbian Academy of Sciences and Arts, the universities and research institutes involved in the organization of the Advanced Ceramics and Applications Conference, and the Serbian Ceramics Society have been very fruitful, with special appreciations to Prof. Vojislav Mitic and his team under the direction of the Serbian Ceramics Society.

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# Flash Sintering of Ceramics: A Short Review

R.I. Todd

**Abstract** “Flash sintering” occurs when an electrical potential difference is applied across a ceramic powder compact and is characterised by an electrical power surge at a specific combination of electric field and temperature, accompanied by extremely rapid densification. The phenomenon is easy to reproduce but the mechanisms responsible remain controversial. This paper reviews the evidence available and examines the thermo-electrical response and densification at high heating rates, concentrating mainly on 3YSZ, which was the first ceramic to be sintered in this way and on which most research has been conducted. The mechanisms which may be responsible for the phenomenon are discussed and areas requiring further investigation are highlighted.

**Keywords** Flash sintering · Yttria stabilised zirconia · Electrical conductivity · Fast firing

## 1 History of Flash Sintering

The earliest report in the open literature of the use of the term “flash sintering” is in 1952 by Hill et al. [1], who describe a process to produce cermets by the application of pressure with rapid heating provided by the direct passage of an electric current through the cermet powder. The authors state that their process was developed from previous work by E.G. Touceda in 1946. The use of electric current to produce rapid sintering is therefore not a new idea and related processes such as spark plasma sintering (SPS) remain in use today.

The flash sintering described in the present paper, however, is a much more recent innovation and was first described in 2010 by Cologna et al. [2] in a paper entitled “Flash sintering of nanograin zirconia in <5 s at 850 °C”. The paper describes a process which is similar to that of Hill et al. [1] in that it involves the use

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of electricity to cause rapid sintering of a powder. However, there are several important differences which distinguish it from the earlier process:

- The process involves sintering without an externally applied pressure.
- The material being sintered is a ceramic which does not conduct electricity at room temperature, in contrast to cermets in which there is a continuous conducting pathway of metallic phase.

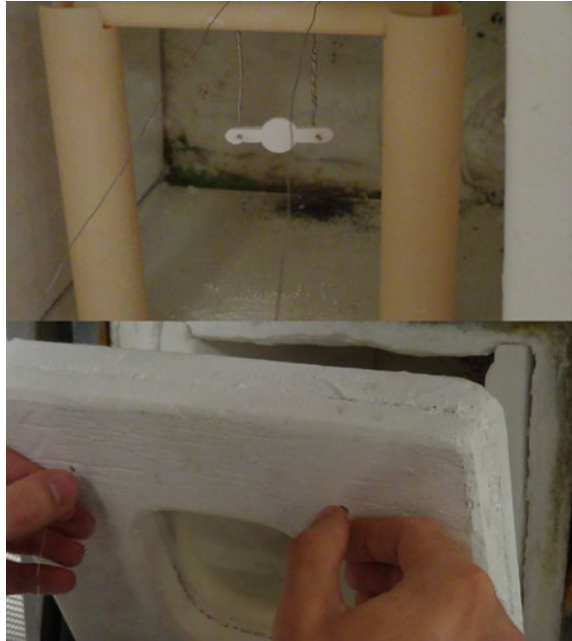
The title of [2] draws attention to two aspects of flash sintering (taken from hereon to refer to the process of Cologna et al.) which are very striking when compared with conventional sintering. The first is that sintering occurs in a few seconds, whereas conventional sintering usually takes several hours or tens of hours. The second is that the temperature quoted is very low for the ceramic in question: the manufacturers (Tosoh, Japan) recommend a temperature of 1300 °C for conventional sintering. However, it should be noted at the outset that the temperature referred to in the title of [2] concerns the furnace in which the specimen is situated, showing that some preheating is necessary before the flash sintering process itself is applied. As will become apparent below, the temperature of the specimen itself is much higher than this during flash sintering because of Joule heating when a current passes through the sample.

Although the original report used the oxygen ion conducting ceramic 3 mol% yttria stabilised zirconia (3YSZ) it is now clear that the process is easy to reproduce and very general as it has also been found to be successful with other grades of zirconia (8YSZ, [3]), proton conductors (Gd-doped BaCeO<sub>3</sub> [4]), electronically conducting oxides (Co<sub>2</sub>MnO<sub>4</sub> [5]), traditional ceramics [6] and covalent semi-conductors (SiC [7]). Most experiments have used direct current, but the process also works with alternating current [4]. Most research to date has concentrated on either (i) expanding the range of materials in order to identify possible applications, (ii) detailed measurements of the conditions under which flash sintering occurs in order to gather evidence for the mechanisms involved [8, 9] or (iii) variations on the experimental setup to investigate other regimes where the use of electric currents in ceramics might be useful [10, 11]. Less research has been reported on the microstructure and properties of ceramics sintered in this way.

## 2 Flash Sintering Experiments

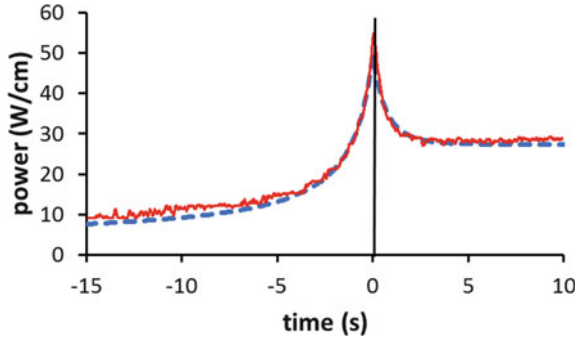
A typical experiment is based on the original report of the phenomenon by Cologna et al. [2] with further information in [12]. YSZ green bodies are suspended in the hot zone of a furnace by two platinum wires, one attached to each end of the specimen. A camera is used to record the dimensional change of the specimen as it sinters. The original report of Cologna et al. [2] used a tube furnace and “dog bone” specimens but different arrangements such as that shown in Fig. 1 using a box furnace and different specimen shape are also successful.

**Fig. 1** *Top* a 3YSZ green body suspended by two platinum wires hung over an alumina frame within a box furnace. *Bottom* the wires are fed through two holes in a furnace door and to a power supply. The door is provided with a window so that the specimen shrinkage can be monitored using a camera



A constant DC voltage,  $V$ , is applied across the specimen by means of the wires and the furnace is programmed to heat up at a constant rate. As YSZ does not conduct electricity at room temperature, nothing happens initially. However, on reaching a critical furnace temperature, the current,  $I$ , and therefore the electrical power dissipation ( $VI$ ), rapidly increase, as shown in Fig. 2 [8].

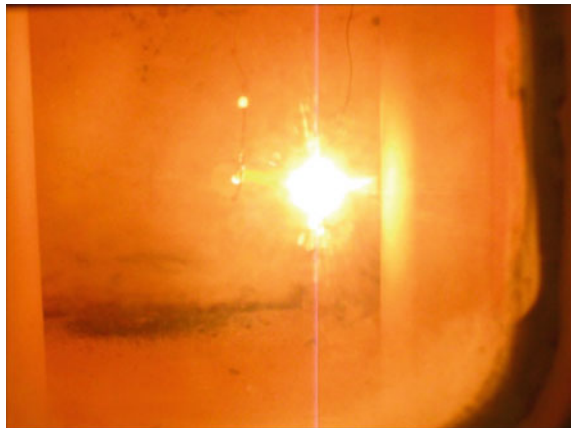
As the power supply can only provide a finite amount of power, it is programmed to switch to constant current when  $I$  reaches some pre-determined value. At this point (time = 0 in Fig. 2), the power dissipation decreases again and eventually levels off at a constant value. It should be noted that this power spike is primarily an artefact of the electrical supply rather than a fundamental response of the ceramic. The camera observations show that sintering takes place during the electrical events described, as shown by shrinkage of the specimen. The main “flash event” takes place over about 15 s and much of the sintering itself typically occurs during a time period of about 5 s around the peak in power dissipation. Radiation emission also accompanies the flash event as shown in Fig. 3. Much of the light emitted is electroluminescence [13] but it is also universally agreed that the specimen heats up because of the electrical power dissipation (Joule heating). The heating can be estimated indirectly using the energy balance between electrical power and heat loss and has also been measured by pyrometers [12] and in situ lattice parameter determination using synchrotron X-ray diffraction [13].



**Fig. 2** Red (solid) line electrical power dissipation in a 3YSZ specimen with an initial applied electric field of 100 V/cm in the furnace of Fig. 1 heating at a rate of 5 °C/min [8]. The power is seen to increase rapidly over a few seconds when the furnace reaches a critical temperature. At time = 0 the current limit of 0.55 A is reached and the current is held constant by reducing the voltage accordingly resulting in a power spike. Blue (broken) line prediction of the finite element model in [8]

Several variations on this basic experiment have been reported. Another important way of identifying the critical combination of furnace temperature and current is to suspend the specimen in a furnace at constant temperature and to gradually increase the voltage until the flash event occurs. Alternatively, voltages in excess of the critical level can be applied continuously or in pulses to stimulate sintering at will [14]. Different electrode materials have been investigated including silver [15, 16] and carbon/graphite [7, 16] and parallel cross-section bars [8], cylinders [7] or discs [11] can also be used with suitable electrodes.

**Fig. 3** Video still of specimen at the flash event in an experiment similar to that shown in Fig. 2



### 3 Possible Mechanisms for Flash Sintering

Flash sintering has proved easy to reproduce and there is wide agreement about the general experimental conditions needed to observe the phenomenon. The possible explanations have proved more controversial and although some areas of consensus are developing, there is no universally accepted mechanism or mechanisms covering the full range of observations which have been reported. Some of the ideas which have been suggested are commented on here.

#### 3.1 *Prior Evidence*

Although flash sintering was first reported in 2010, there are previous reports on the effect of electric fields on the sintering of ceramics. Most of these concern the application of much lower electric fields than those required to initiate the flash event of Figs. 2 and 3 and include the substantial literature published during the last 20 years on “Spark Plasma Sintering” (SPS), also known as Field Assisted Sintering (FAST), in which powders are densified under pressure in a conductive cylindrical die (usually graphite) by passing a high current at low voltage from the top ram to the bottom ram. The relevance of the electric field in SPS is itself controversial and the present review will not repeat the arguments involved.

There are, however, a few reports of pressureless sintering in 3YSZ with simultaneous application of electric fields which provide a good starting point for the discussion of flash sintering. Ghosh et al. [17] reported in 2009 that the application of a DC field of 4 V/cm significantly suppressed grain growth in 3YSZ during annealing. The importance of these results is that the experimental geometry was such that experiments could be conducted which were identical in every way *except* for the presence or absence of the electric field. The results therefore provide indisputable evidence that electric fields have a measurable influence on high temperature microstructural development, at least in 3YSZ. Related work [18] also showed that sintering occurred more rapidly at a given temperature in the presence of an electric field than without it and this was attributed, at least in part, to the suppression of grain growth. Whilst the results are interesting, however, the acceleration produced did not enable sintering in the timescale of a few seconds and so although this effect must contribute to the success of flash sintering, additional explanations must be sought.

#### 3.2 *Local Heating of Grain Boundaries*

In the original report of flash sintering, Cologna et al. [2] reviewed possible explanations for the rapid sintering and suggested that local Joule heating at the

particle-particle contacts because of their high electrical resistance relative to the grains may accelerate grain boundary diffusion sufficiently to cause the rapid densification observed. Chaim [19] has extended this idea to include local melting of the grain boundaries, giving further possibilities for the acceleration of sintering by including liquid phase sintering mechanisms.

These ideas have been criticised, however, on the basis that they take no account of heat flow [8]. The thermal diffusivity of 3YSZ is such that temperature excursions travel about  $1\ \mu\text{m}$  in  $1\ \mu\text{s}$ . In submicron powders such as those used in flash sintering, therefore, local heating at particle-particle contacts cannot be sustained over the timescale of several seconds in which flash sintering takes place. This appears to rule out the simple idea of local heating and/or melting but, bearing in mind the results in the previous section, it does not rule out the possibility if some other mechanism, yet to be identified, occurring in response to the concentration of current or electric field at the grain boundary.

### ***3.3 Nucleation of Avalanches of Lattice Defects***

Also in the survey of possible mechanisms in the original report of flash sintering [2], the novel possibility of the production of lattice defects such as Frenkel defects was suggested. This has since been developed further to postulate that the Frenkel pairs occur in an avalanche and ionise into charge neutral defects and electron-hole pairs [20, 21].

The main attraction of this proposal is that it offers a single mechanism explaining all, or nearly all, of the observed aspects of flash sintering in YSZ: the lattice defects would increase diffusion rate, offering fast sintering and the electron-pairs would explain both the high electrical conductivity observed at the flash event and, by recombination, the photoluminescence. The idea of nucleation being necessary is also consistent with the so-called “incubation time” for flash sintering. This refers to the observation of a time delay after the application of an electric field greater than the critical value at a given furnace temperature before the flash event takes place [21].

It must also be stated that the fact that this proposal offers a unified explanation is the main argument in its favour; details of the proposed mechanism and in particular the energetics of the defects and the kinetics they might produce, are lacking. It is also not clear how such a lattice-specific mechanism would be consistent with the generality of the effect, which is also seen in covalent semiconductors such as SiC, for instance [7].



### 3.4 Thermal Runaway of Joule Heating

It is evident from Fig. 2 that significant power is already being dissipated in the specimen well before the flash event. That 3YSZ is a good ionic conductor at the furnace temperatures at which flash sintering takes place is well known, and its resistivity shows the negative temperature coefficient (NTC) behaviour shown by essentially all ceramics—whether ionic, electronic or semi-conducting—under the relevant conditions. At constant voltage, this gives the possibility of classical thermal runaway, an effect well known in many physical situations, including ceramic thermistors. The effect occurs as a positive feedback loop in which as the temperature increases due to Joule heating, the electrical power dissipated  $V^2/R$  increases because the resistance  $R$  decreases with temperature, which leads in turn to an increased Joule heating rate, and so on.

The present author and co-workers examined this possibility [8] and, assuming a uniform temperature within the specimen, developed an analytical expression for the combination of furnace temperature and electric field which would lead to thermal runaway, i.e. the flash event. In [8], the expression was developed for a circular cross section but the equivalent expression for a specimen with a uniform cross-section of arbitrary shape is as follows:

$$E_{crit}^2 = \frac{4P\varepsilon\sigma\rho_0R}{AQ}(T_0 + \Delta T_{crit})^5 \exp\left(\frac{Q}{R(T_0 + \Delta T_{crit})}\right) \quad (1)$$

in which for  $\Delta T_{crit} \ll T_0$ :

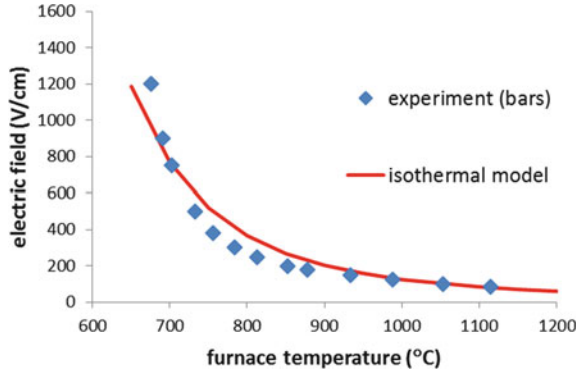
$$\Delta T_{crit} \approx \frac{RT_0^2}{Q - 5RT_0}. \quad (2)$$

In these equations,  $E_{crit}$  is the critical electric field required to cause thermal runaway/the flash event with a furnace temperature  $T_0$ ,  $P$  and  $A$  are the perimeter and area respectively of the specimen cross section,  $\rho_0$  and  $Q$  are the pre-exponential and activation energy in the inverse Arrhenius expression describing the resistivity,  $R$  is the gas constant,  $\varepsilon$  is the emissivity,  $\sigma$  is Stefan's constant and  $T_0 + \Delta T_{crit}$  is the specimen temperature at runaway.

The model was tested by using the electrical data taken *before* the flash event in constant voltage flash sintering experiments to characterise the resistivity ( $\rho_0$  and  $Q$ ) and then to predict the  $E_{crit}$  versus  $T_0$  relationship using Eqs. (1) and (2). The results are shown in Fig. 4. Considering the simplicity of the model, the agreement is very good.

A numerical (finite element) model allowing variation of temperature within the cross section and predicting the development of electric parameters and specimen temperature with time was also developed in [8] and used the same electrical property data. An example prediction of this model with experiment is shown in Fig. 2 along with the experimental result. It shows near-perfect agreement with

**Fig. 4** Predicted and experimentally measured relationship between the electric field and furnace temperature at the flash event for the isothermal model of Eqs. 1 and 2 with 3YSZ as the ceramic used. Data from [8]



experiment demonstrating that the increase in current and power in the lead up to the flash is a consequence of rapid specimen heating combined with the NTC resistivity behaviour of the ceramic.

It is important to emphasise that the model predictions in Figs. 2 and 4 are absolute predictions with no adjustable parameters and use materials properties measured before the flash event. The excellent agreement with experiment coupled with the fact that the models also successfully predict details of the phenomenon such as the incubation behaviour, the localisation of current and temperature under conditions of high limiting current and the approximately constant power density at the flash event are strong arguments in its favour. When the additional argument that this is an entirely classical effect which is *expected* to occur is considered, there can be little doubt that the main electrical and thermal characteristics of flash sintering are a consequence of classical thermal runaway of Joule heating. A consensus seems to be building around this view and the same conclusion has been reached with other materials: Zhang et al. have independently reached the same conclusion for ZnO [22] and the flash conditions in  $\text{Al}_2\text{O}_3/\text{TZP}$  composites [23],  $\text{BaTiO}_3$  [24] and  $\text{Al}_2\text{O}_3$  [16] can be predicted using the same principles.

Although this understanding of the electrical and thermal behaviour during flash sintering provides a good foundation on which to build, it is important also to recognise that further research is needed in this area. First, it should be pointed out that the models reviewed are phenomenological: the origin of the electrical properties measured is not fully understood. In [8], for instance, the activation energy for resistivity in 3YSZ was significantly higher than literature values measured under low voltage, low current conditions which are very different to those occurring during flash sintering. Much of this can be attributed to the sintering taking place concurrently with the heating of the specimen, which would have the effect of reducing the resistivity more rapidly with temperature than the underlying mechanism would suggest. However, given the fact that 3YSZ is known as an ionic conductor, it seems inconceivable that sufficient oxygen could be collected and ionised at the point contacts between the wire at the cathode and the specimen to enable currents of 0.5 A or more to be passed purely by this mechanism. A detailed

explanation of the electroluminescence seen in YSZ [13] is also lacking and there are other observations such as unexpected phase changes during flash sintering [25, 26] which are yet to be understood. This suggests that novel crystal or electronic defect processes may be involved in the conduction of electricity under these unusual conditions, even if the thermal runaway explanation for the flash event means that the dramatic avalanches discussed in Sect. 3.3 are not required.

### 3.5 *Mechanisms for Rapid Sintering*

Another area where further research is needed concerns the rapid sintering observed during and after the flash event. The obvious starting point is that high specimen temperatures can increase the sintering rate and it is clear from the previous section that the specimen temperatures far exceed the furnace temperatures used. Raj [12] investigated this possibility by extrapolating conventional sintering results and concluded that a temperature of 1900 °C would be needed to sinter 3YSZ to high density in 5 s, whereas the specimen temperature in flash sintering was estimated possibly to be as low as 1250 °C. The conventional data used by Raj were approximate; more precise data from the literature have also been used [8] and although the required temperature predicted is then much lower, at 1625 °C it remains significantly above the experimental temperatures, even allowing for the considerable uncertainty in specimen temperature resulting from the difficulty in measuring it (the use of thermocouples in contact with the specimen is incompatible with the potential differences involved in flash sintering and the temperature gradients thought to exist in the specimen make pyrometry and other surface measurement techniques unreliable).

First, the possibility of matter transport by novel lattice defects such as those reviewed in Sect. 3.3 cannot absolutely be ruled out, as discussed in the previous section. However, in the absence of any clear theoretical or experimental evidence for such defects (other than the need to explain the rapid sintering), this possibility will not be discussed further here.

The local heating and melting of the particles at contact points is also not considered further for the reasons given in Sect. 3.1. However, other effects at the boundary may play a role, especially given the proven effect of electric fields on grain growth. It is also noted that the rapid heating in flash sintering may allow liquid phases to form by other means such as the melting of impurities that might otherwise have been incorporated within the grains or have formed higher melting point reaction phases with them during slow heating.

Finally, it is important to point out that sintering is a complicated process that cannot be simply extrapolated using a single Arrhenius expression. It has been known for over 50 years that rapid heating alone, also known as “fast firing”, without the involvement of electricity, can enable an acceleration in sintering. As long ago as 1966, Vergnon et al. [27] showed that alumina powder sinters to a higher density when the initial heating is faster, even when the dwell temperature is

the same. These authors attributed this to the suppression of grain growth at high heating rates. Later, other researchers also reported rapid sintering with high heating rates [28–30] and the results were rationalised in terms of the different activation energies of coarsening mechanisms such as neck growth, as well as the grain growth of Vergnon et al., which compete with densification. Rapid heating to high temperature avoids intermediate temperatures where low activation energy processes such as the surface diffusion responsible for neck growth with densification dominate [29–31]. This “fast firing effect” is an established fact and must contribute to the rapid sintering in flash sintering. Whether the ultra-fast heating in flash sintering can extend the effect to the ultra-fast densification observed remains to be seen.

More recently, it has been tentatively suggested by Zhang et al. [32] that very rapid heating may not allow time for the newly formed grain boundaries between particles to reach their equilibrium, low energy structure. The less compact, metastable structures may have higher diffusion coefficients. Little investigation of this possibility has been conducted to date, however, and it remains a speculative suggestion.

## 4 Conclusions and Final Comments

Flash sintering is a relatively new method for sintering ceramics rapidly—in a matter of a few seconds once the specimen is preheated. It is easy to reproduce and is exhibited seemingly by any ceramic capable of conducting electricity at high temperature. There are clear commercial possibilities owing to the high speed of the process and the lower energy requirement—only the component is heated to the sintering temperature.

The electrical and thermal response is explain well in terms of conventional thermal runaway of Joule heating. However, the mechanistic details of electrical conductivity of ceramics under the relevant conditions of high temperature, high electric field and high current have hardly been explored and further research is needed in this area.

The reasons for the rapid sintering rate also need further investigation. Although many suggestions have been made, none has gained widespread acceptance. The well-known “fast firing” effect must contribute to the acceleration in sintering but the extent of its contribution has not been established. Other suggestions remain speculative.

As well as the need for fundamental investigations to establish the physical mechanisms mentioned above, there are several issues of more practical importance which need further work. These include improved methods for the measurement of temperature during flash sintering, more investigation of the microstructure and properties of flash sintered ceramics, and finally the development of more practical systems for supplying the electric field and current so that commercial application can be realised.

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# Ceramic Matrix Composites for High Performance Friction Applications

Walter Krenkel and Nico Langhof

**Abstract** Ceramic Matrix Composites (CMC) show due to their fiber reinforcement high strength, thermal shock resistance and damage tolerance, a low coefficient of thermal expansion (CTE) and a partially porous and micro-cracks containing matrix. Hence, C-fiber reinforced silicon carbide materials (C/SiC resp. C/C-SiC), manufactured by the LSI (Liquid Silicon Infiltration) process, are very suitable for friction applications, e.g. for brake discs and pads, because of their low wear rates and high coefficients of friction (COF). Fundamental studies and ongoing investigations are the basis for the introduction of fiber reinforced ceramic brake discs for passenger cars since more than 10 years. Today, C/SiC friction materials can be found in emergency brakes for elevators, conveying systems and passenger cars. With respect to the selected friction couple, the tribological performance remains on a high level over a large range of sliding speed and braking pressure. In order to develop C/SiC lifetime brakes for passenger cars, the corresponding brake pads have to be modified appropriately as well. Within a certain friction system, the C/SiC ceramic brake discs withstand a mileage up to 300,000 km, compared with about 70,000 km of grey cast iron rotors. The economic success of these innovative, damage tolerant ceramics depends on the further reduction of the fabrication costs, which are considerable higher, compared to the competing metallic materials. This article describes the technological steps in the development of ceramic friction materials and the current status. It gives an overview about the most important, forthcoming challenges in terms of the material's development and processing.

**Keywords** Friction · Ceramic brakes · C/SiC · Ceramic matrix composites · Tribology

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## 1 Introduction

Carbon fiber reinforced ceramic friction materials are promising for several engineering applications, especially if lightweight, high power densities and high temperature stability are required. Therefore, these materials are suitable candidates for e.g. transportation systems in the aerospace sector, for railways and automotive applications. In general, all engineering components that contain translational or rotational inertia masses and other devices that have to be decelerated by an incorporated brake system are interesting applications of ceramic matrix composites. Nowadays, braking of huge amounts of kinetic energies can be realized by the application of regenerative brakes. Nevertheless, a secondary emergency brake, which is based on friction, is still required for the case that the primary brake system fails.

In the field of Ceramic Matrix Composites, Carbon/Carbon materials (C/C) are already in use for friction applications in airplanes and Formula One race cars, since several decades [1–4]. However, C/C shows some drawbacks, in terms of their low COF at low temperatures and high humidity resp. under “cold” and “wet” conditions. Therefore, this material is not suitable for lifetime brakes in passenger cars or further engineering applications. Only at temperatures above 400 °C carbon/carbon brakes are favorable and show very promising performances. However, such temperatures are accompanied with high wear rates due to the oxidation of carbon. Based on these drawbacks and the time and cost consuming fabrication process, C/C brakes are not suitable for service brake applications.

Due to the replacing of the carbon matrix by SiC in C/SiC composites, a material is obtained, which shows a significantly enhanced wear and oxidation resistance compared to C/C. Furthermore, the tribological performance of the material is improved as well. C/SiC is a material with open porosities < 3 %. The infiltration of liquid silicon occurs under vacuum conditions into a porous carbon/carbon preform without the requirement of any external pressure, only by capillary forces and the good wetting behavior of silicon on carbon. The excess of the supplied silicon, which means, more than the required stoichiometric amount to form SiC, causes the formation of an almost dense material including some residual free silicon. Originally, the Liquid Silicon Infiltration process was developed to produce C/SiC for thermal protection systems in space shuttles and similar reentry vehicles in the aerospace sector [5].

Figure 1 shows the flowchart of the LSI-process, which consists of three main steps. Within the first step C-short fiber bundles are mixed resp. C-fiber fabrics are laminated with a phenolic resin, e.g. Novolac. The addition of fillers, e.g. graphite powder enables the modification of the desired frictional properties. This compound is warm pressed and the CFRP evolved at temperatures up to 300 °C and pressures up to 5 MPa. During the second step, the CFRP is carbonized under inert conditions at temperatures beyond 900 °C. Due to the pyrolysis and partial degradation of the

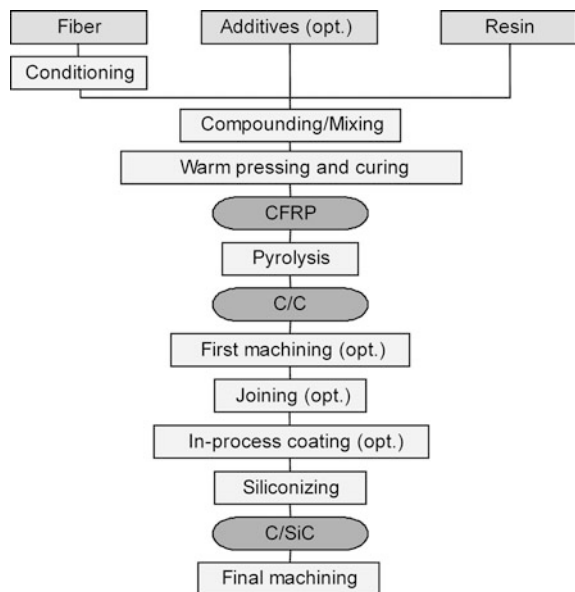


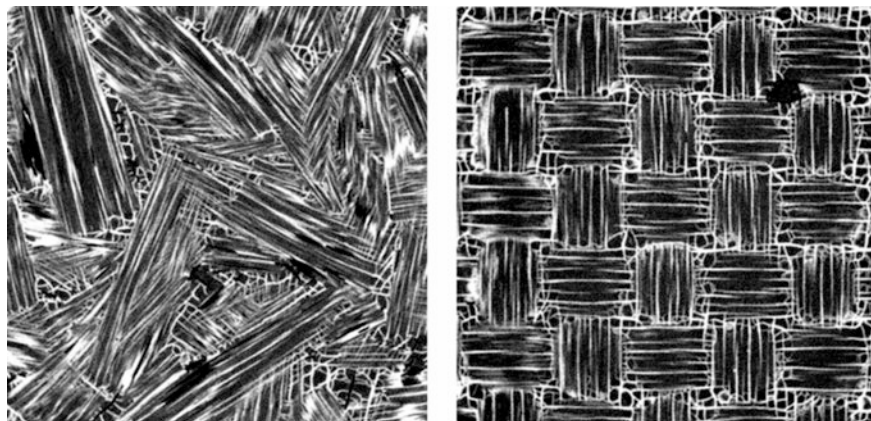
phenolic resin, the matrix shrinks and loses about 50 % of its mass. The shrinkage and the fiber matrix bonding must be tailored, in order to prevent a debonding of the matrix from the C-fibers. The resulting C/C body contains between 20 and 30 % of open porosity. The cracks form an interconnecting network of narrow channels between distinct C/C-segments in the microstructure. Within the third step, the porous C/C preform is infiltrated with liquid silicon under vacuum and temperatures above 1420 °C. Finally, the liquid Si reacts with the solid amorphous carbon matrix to form SiC in a diffusion controlled process.

C/SiC consists of three phases, carbon (fibers and matrix), SiC (matrix) and residual silicon (matrix). Typical microstructures of different C/SiC composites are shown in Fig. 2. If a dense friction material is desired, like for the most applications, C/SiC composites contain about 5 vol. % free silicon. This amount is required to compensate the 30 % lower molar volume of SiC compared to the sum of the molar volumes of Si and carbon. However, free silicon can be prevented, due to the addition of the stoichiometric amount of silicon, regarding to the existing amount of carbon, which should be converted into SiC. The final material is porous and show about 5 % open porosity and no residual silicon. Absolutely dense C/SiC materials without any free silicon can't be obtained by the LSI-process. Knowing these specific relations, C/SiC friction materials can be tailored to a certain degree towards the requirements of the application.

The braking energy which have to be absorbed by a brake disc and/or pad are exemplarily summarized in Table 1 for different transportation systems, where

**Fig. 1** Flowchart of the Liquid Silicon Infiltration process (LSI) for the manufacturing of C/SiC friction materials





**Fig. 2** C/SiC microstructures with C-short fibers (*left*) and C-fabric reinforcement (*right*) perpendicular to the press direction, i.e. the frictional surfaces are shown; carbon fibers (*black*); SiC and Si (*white*) [Fraunhofer-HTL]

ceramics are already in use or under investigation. Despite of the large numbers of brake discs in trains and airplanes, the energies per disc in these systems are remarkably higher compared to other service brakes in passenger cars or in emergency brakes for elevators or conveying systems. Therefore, each application requires a different, specific modified C/SiC friction material.

Some fundamental aspects of these material modifications will be discussed in the forthcoming chapter.

**Table 1** Braking energies of different high performance friction applications (service and emergency brakes) [24]

|                               | Train<br>ICE1 | Aircraft<br>Boeing 777 | Automotive<br>Porsche GT2 | Elevator<br>(emergency)<br>Schindler 700 | Crane<br>(emergency)<br>Mayr roba-stop |
|-------------------------------|---------------|------------------------|---------------------------|--|--|
| Max. speed<br>(m/s)           | 91.7          | 72.2                   | 88.9                      | 13.8                                     | 30                                     |
| Mass ( $10^3$ kg)             | 440           | 208                    | 1.7                       | 18                                       | 3.1                                    |
| Deceleration<br>( $m/s^2$ )   | 1.3           | 2.4                    | 14.5                      |  |  |
| Brake energy<br>(MJ)          | 1850          | 542                    | 6.7                       | 1.7                                      | 1.4                                    |
| No. of brake<br>disks         | 192           | 48                     | 4                         | 8  | 1                                      |
| Energy per<br>brake disk (MJ) | $7.2^1$       | $4.5^2/20^3$           | 1.7                       | 0.21                                     | 1.4                                    |

<sup>1</sup>75 % of brake energy

<sup>2</sup>40 % of brake energy

<sup>3</sup>Emergency (RTO = Rejected Take-Off)

## 2 Development of C/SiC Materials for High Performance Friction Applications

The development of C/SiC composites for braking systems has started in the early 90s of the former century and shows a successful spin off from space to terrestrial applications. In the beginning, the feasibility and manufacturing of prototypes for railway brake discs were in the focus of the research activities [6]. One big challenge was the transfer of the existing technology from thin-walled aerospace structures (thickness 3–6 mm) to large scaled (diameter up to 640 mm) and thick-walled components (up to 60 mm thickness) for brake rotors. Thereby, it is required to remain the mechanical properties and the quality of the materials.

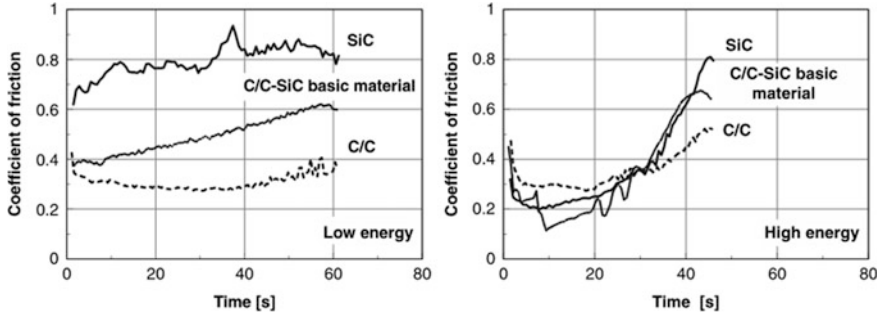
In 1994 the German Aerospace Center in Stuttgart (DLR) started to collaborate with Porsche, in order to develop C/SiC brake pads and discs for passenger cars [7]. First tests showed the superior tribological and thermomechanical properties compared to grey cast iron and C/C. Nevertheless, the design and manufacturing have to be developed and some milestones in the material's improvements are described in the following.

### 2.1 *Improvement of the Transversal Thermal Conductivity ( $\lambda_{\perp}$ ) to Stabilize the Coefficient of Friction (COF) of the C/SiC Materials*

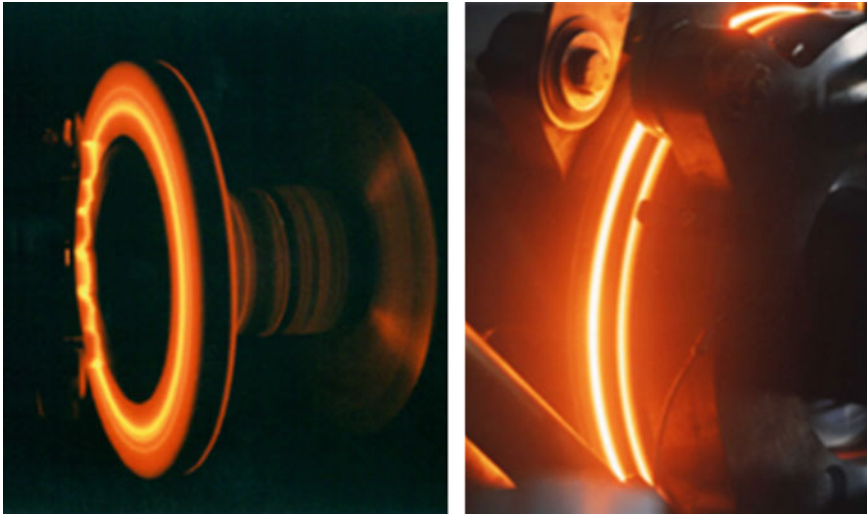
In principle, monolithic SiC is very suitable for friction applications, due to its high wear resistance and very high COF. However, the very brittle failure behavior prevents the application of monolithic SiC in brakes. In particular, thermal shocks are very critical and make SiC unfavorable for these safety components. Nevertheless, SiC within the matrix of damage tolerant C/SiC is very important, in order to enhance the COF and to increase the wear resistance, compared to the C/C material.

During tribological studies at moderate conditions and low braking energies on a disc-on-disc tribometer, it was found, that the COF of C/SiC is a superposition of the COFs of pure C/C and monolithic SiC (Fig. 3). At higher friction energies, this relation is less obvious and the COFs for all three materials are similar [8, 9].

First tests show an overheating of the frictional surfaces and the heat transfer into the volume of the rotor was not sufficient (Fig. 4). The main reason for this behavior was the low thermal conductivity, perpendicular to the fiber axis ( $\sim 9$  W/mK), of the 2D-reinforced C/SiC material. Due to some modifications of the microstructure and the phase composition, the thermal conductivity was increased significantly. One approach was the increase of the amount of SiC in the matrix by decreasing the content of the fibers, which increases the Si-uptake and enhance the SiC content and the density of the C/SiC materials (Figs. 5 and 6).



**Fig. 3** Coefficient of friction (COF) of 2D-fabric reinforced C/SiC, monolithic SiC and C/C at low braking energies, resp. power intensities ( $v = 16$  m/s,  $p = 0.1$  MPa, *left*) and at higher braking energies ( $v = 16$  m/s,  $p = 0.35$  MPa, *right*)



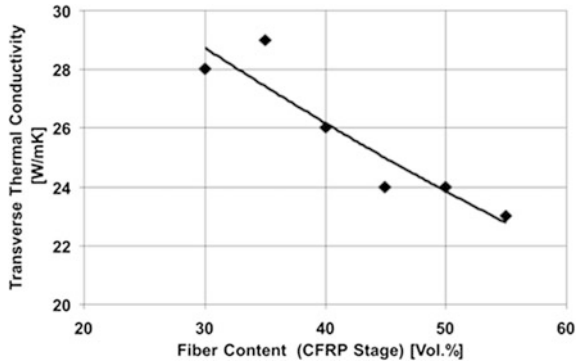
**Fig. 4** High temperatures on the frictional surfaces due to low transversal thermal conductivity of fabric reinforced C/SiC [Knorr-Bremse, DLR]

Another way was to apply carbon fibers with a higher thermal conductivity, e.g. graphite-based fibers [10].

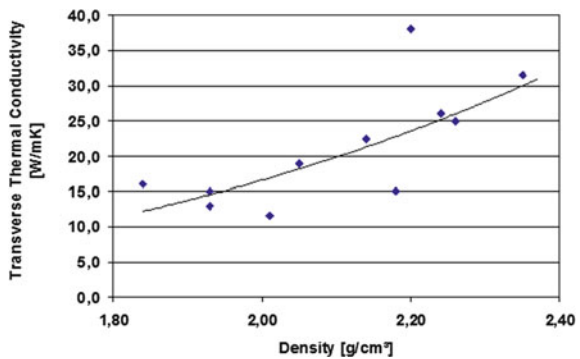
On the one hand, the thermal conductivity increases with the decrease of the fiber volume content and the increase of the density. On the other hand, the mechanical strength and the fracture toughness decrease. Therefore, the microstructure and the composition of C/SiC have to be balanced between mechanical and thermal requirements of the desired application.

In order to reach high thermal conductivities of about 40 W/mK, the fiber volume content is between 30 and 50 % and the open porosity below 5 %. Due to the

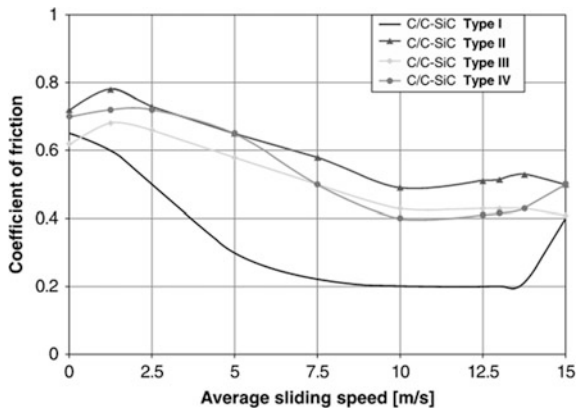
**Fig. 5** Transversal thermal conductivities of C/SiC versus fiber volume content (carbon short fiber reinforcement; measured at 50 °C)



**Fig. 6** Transverse thermal conductivity of C/SiC versus density (carbon short fiber reinforcement; measured at 50 °C)



**Fig. 7** COF in dependence on the average sliding speeds of several C/SiC materials, with different thermal conductivities (*Type I* low thermal conductivity with 2D-fabric reinforcement; *Type II-IV* high thermal conductivity with graphite-fibers, high SiC contents resp. some additional fibers in transversal direction) [10]

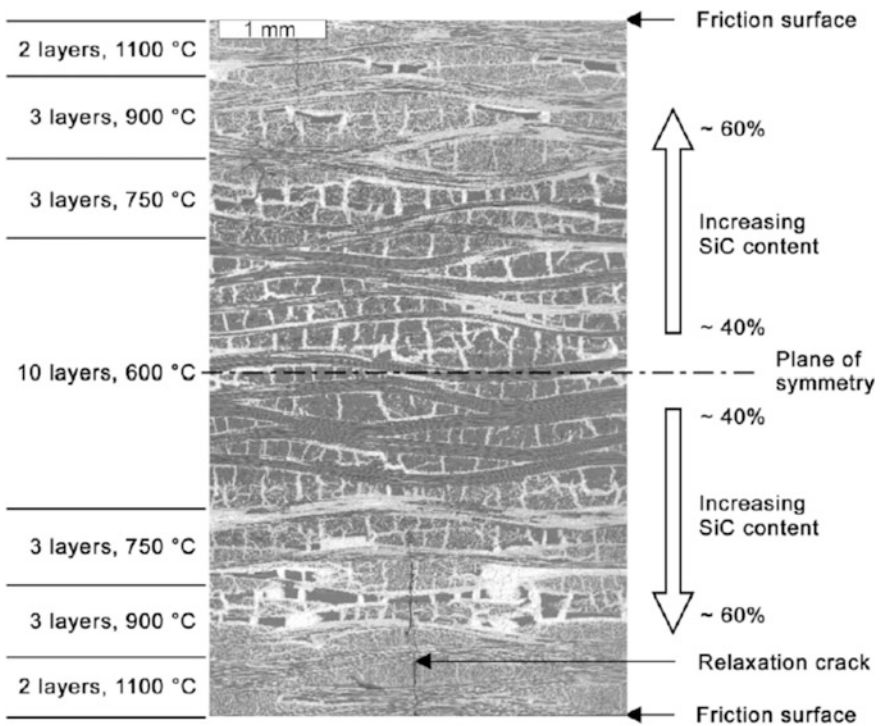


favorable thermal conductivity, the friction-induced heat is transferred easily from the surface into the main body of the ceramic C/SiC friction material. Hence, overheating of the surface does not occur and the COF is now much more stable (Fig. 7). The wear rate remains constant, unless the higher thermal conductivity [11].

## 2.2 Lower Wear Rates by Modifying the C/SiC Friction Materials

C/SiC materials show a significantly higher wear resistance, compared to C/C. Nevertheless, for the application in lifetime service brakes, the wear rates were still too high. The most promising approach to improve the wear stability is to increase the SiC content on the frictional surfaces of C/SiC brake disks or pads.

Two different strategies were developed successfully. By one approach, the gradation of C/SiC laminates with a steadily increasing SiC-content from the center towards the friction surface is suitable for short-term applications, like emergency brakes for elevators or conveying systems. The CFRP-laminate comprises for example different thermal pretreated C-fiber fabrics. With an increasing of the pretreatment temperature, the carbon fibers convert more and more to SiC during the siliconizing step. In order to avoid deformations due to the mismatches of the coefficients of thermal expansion, a symmetric lay-up of the fabrics is required (Fig. 8).



**Fig. 8** Cross section (thickness ~ 6 mm) of a graded C/SiC friction pad, developed for emergency brakes in high-rise elevators [16]