

Ceramics and colloids

A. Testino

Sintering 3

References:

- J. Barton, P. Bowen, C. Carry & J.M. Haussonne - Les Céramiques. Les Traités des Matériaux, Volume 16, PPUR (2005)
- M.N. Rahaman - Ceramic processing and sintering. Taylor & Francis. Second edition (2003). Chapters 7-10
- A. Leriche, F. Cambier, S. Hampshire – Sintering of Ceramics. Reference Module in Materials Science and Materials Engineering (2017)
- M.G. Randal, P. Suri, S.J. Park – Review: liquid phase sintering. J.Mater. Sci. 44, 1-39 (2009)
- W. D. Kingery - Densification during Sintering in the Presence of a Liquid Phase. I. Theory, J. Appl. Physics, 30, 302-306 (1958)

Summary Week 12-13-14

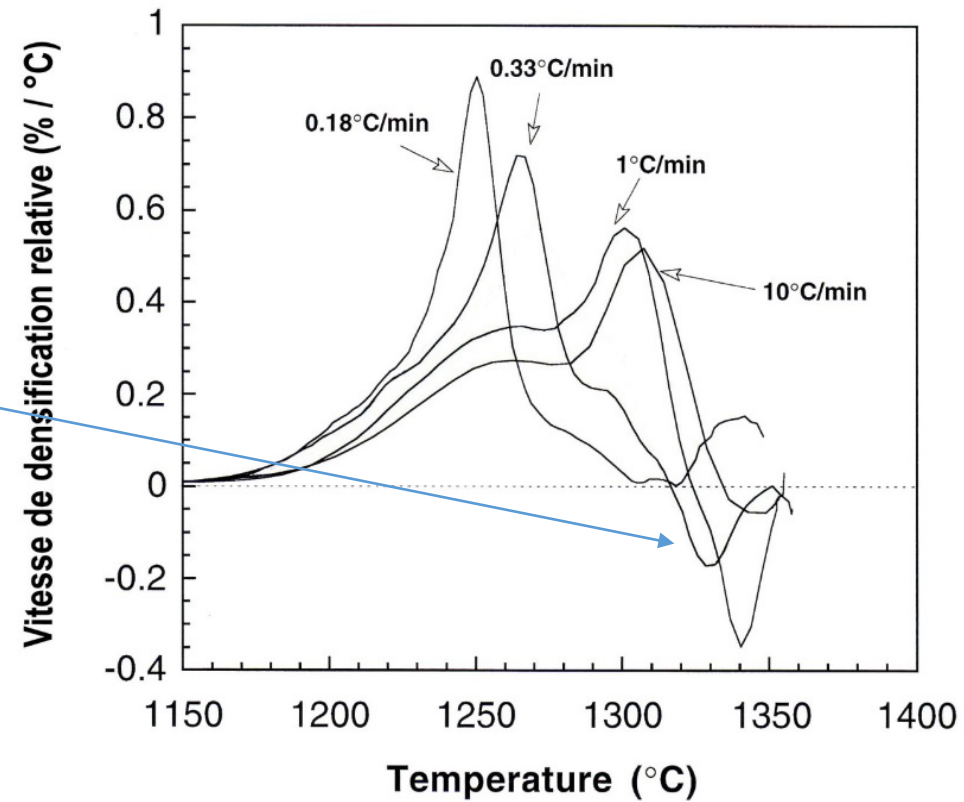
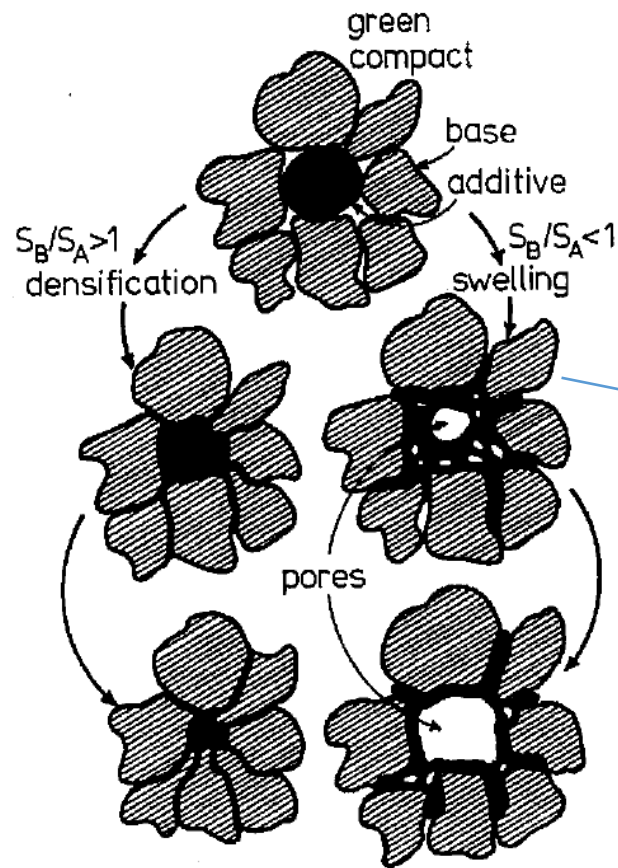
1. Sintering fundamental (10)
2. Solid state sintering (16)
3. Grain growth & microstructure (22)
4. Liquid phase sintering (13)
5. Examples and practice (11)

Week 14

Sol-gel and thin films

Swelling

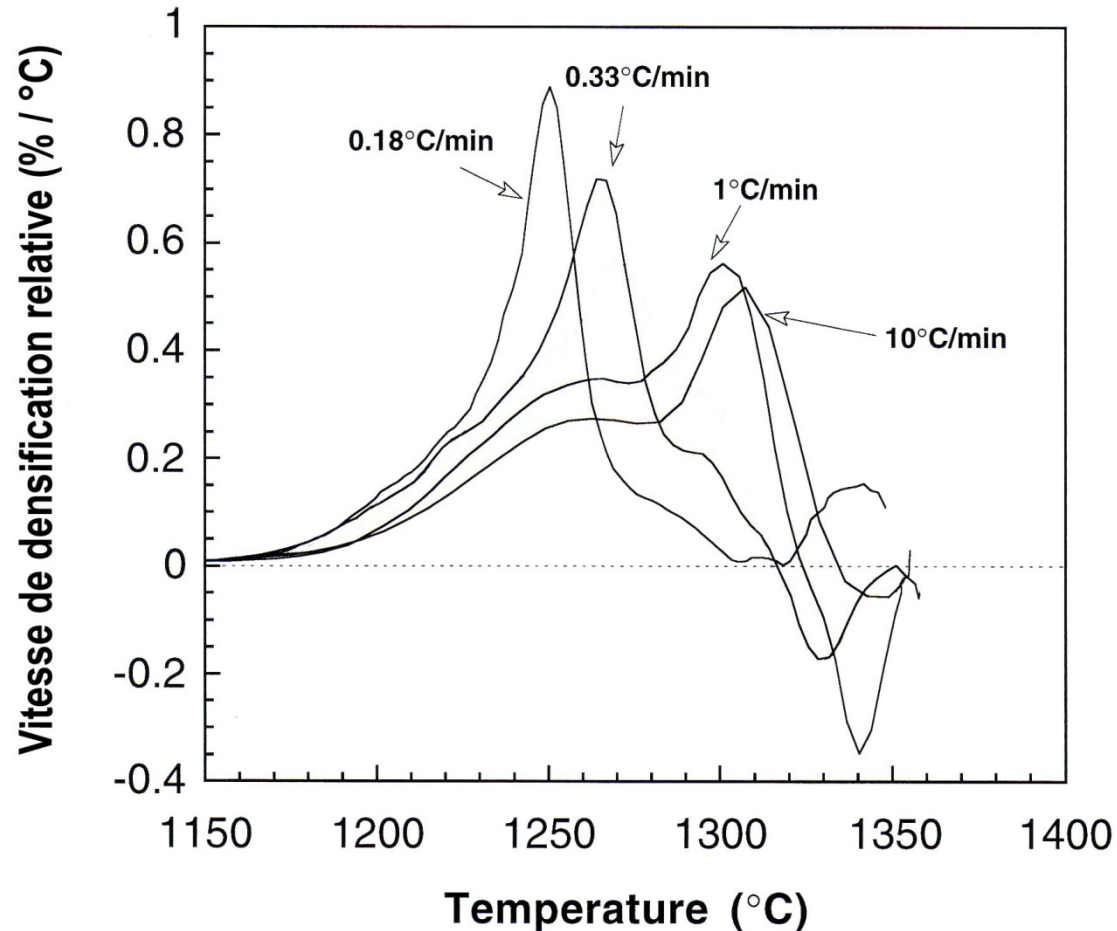
As discussed, good solubility of the solid in the liquid lead to densification and it is essential for LPS. Nevertheless, too high solubility should be avoided because it leads to transient liquid phase and *swelling*.



Solubility (generally) increases with T and too high temperature may lead to swelling.

FIGURE 10.10 Schematic diagram comparing the effects of solubility on densification or swelling during liquid-phase sintering. (From Ref. 15.)

Heating rate effect



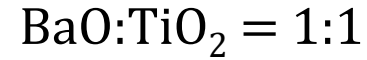
Fast heating rate is not always the best approach.

Sometimes, excellent results can be obtained by sintering close to the max shrinkage rate.

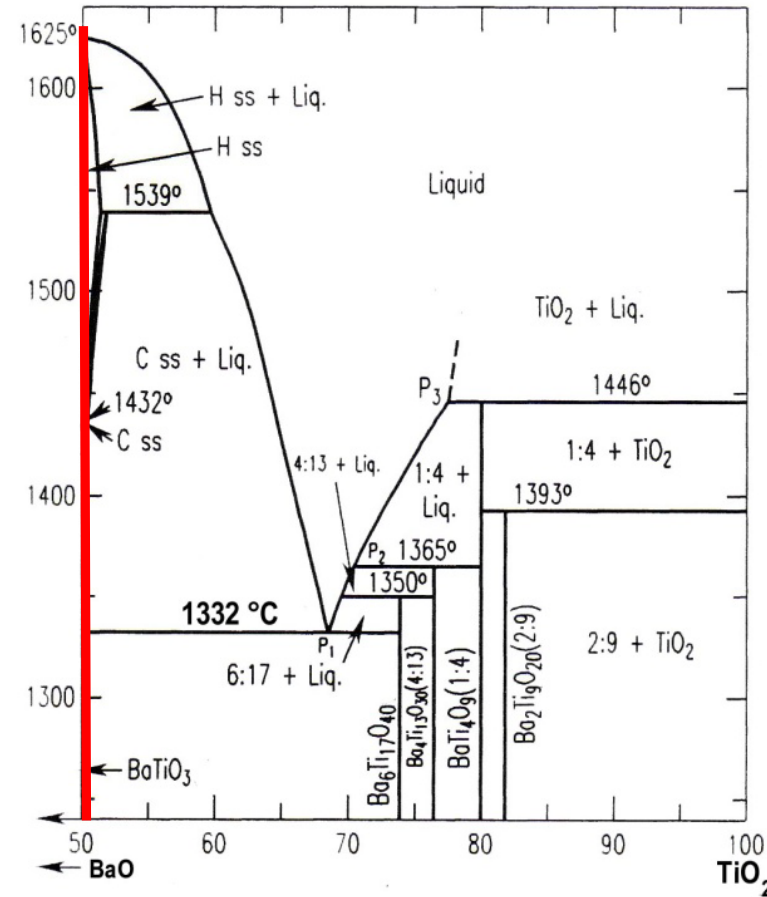
As for dopants, the formation of liquid phase may be influenced by the grain size (small grains can accommodate more defect as limited stoichiometric deviations)

Relative densification rate of green body undergo sintering at 4 different heating rate. Negative speeds corresponds to desintering (swelling). Example: BaTiO₃

Phase diagram and liquid phases



e.g. by solid state synthesis
 $\text{BaCO}_3 + \text{TiO}_2 \rightarrow \text{BaTiO}_3 + \text{CO}_2$



Remember:

- lever rule;
- eutectic point.

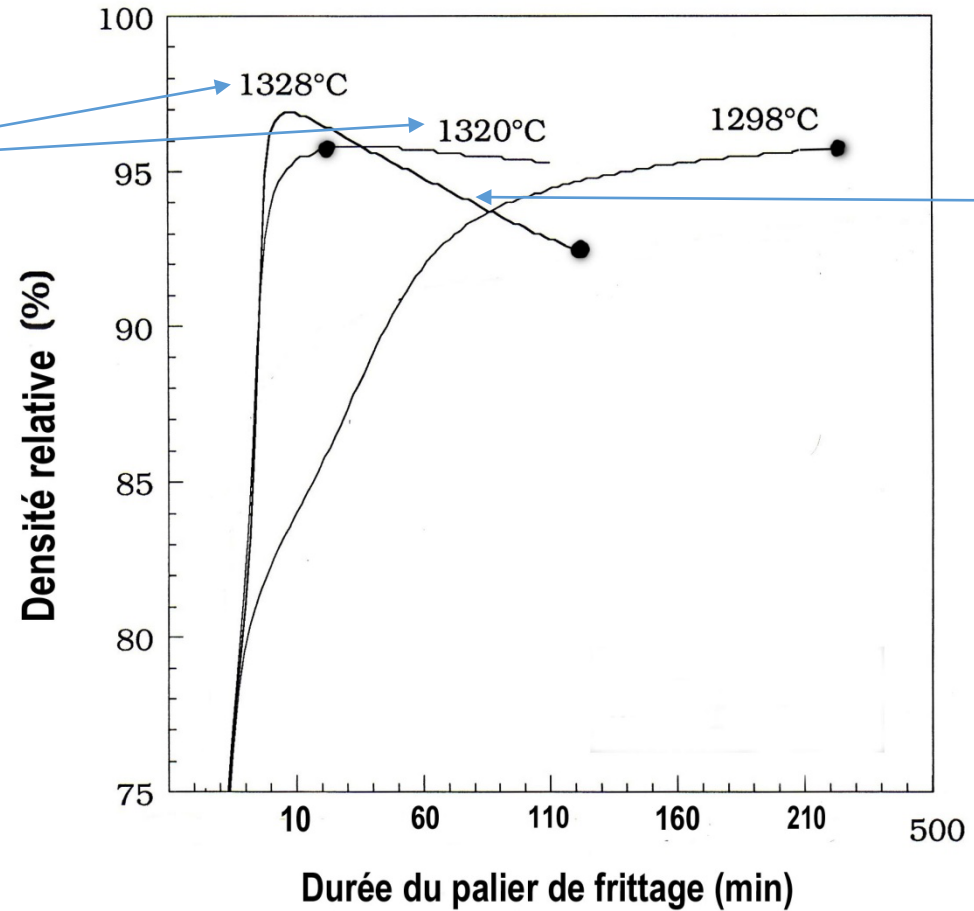
Barium titanate (BaTiO₃) phase diagram: liquid phases can be formed

Max sintering temperature

$$8/1328 \Rightarrow 0.6\%$$

Only 0.6% difference
generate a huge difference
on sintering because close to
liquid phase formation!
Always check phase diagram...

Accurate thermal control;
Accurate T calibration;
Homogeneity in the oven.



Swelling (see LPS)

Sintering curves at isothermal condition. Heating rate 3.3 K min^{-1} .
For $T > 1315 \text{ }^\circ\text{C}$, desintering (swelling) occurs.

Master Sintering Curve (MSC)

What is the best heating profile? Since the thermal history define the microstructure and the microstructure define the properties, to a specific application an optimal sintering process corresponds.

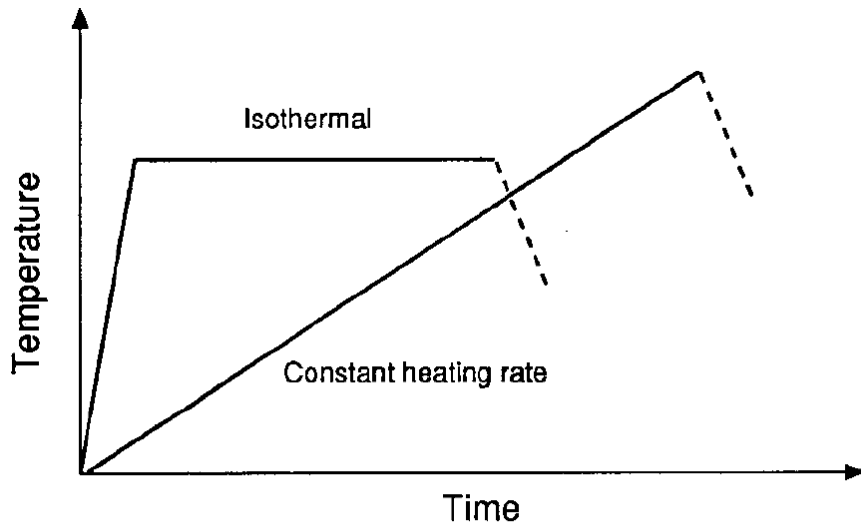


FIGURE 12.6 Sketch of the temperature–time schedule for isothermal sintering and constant heating rate sintering.

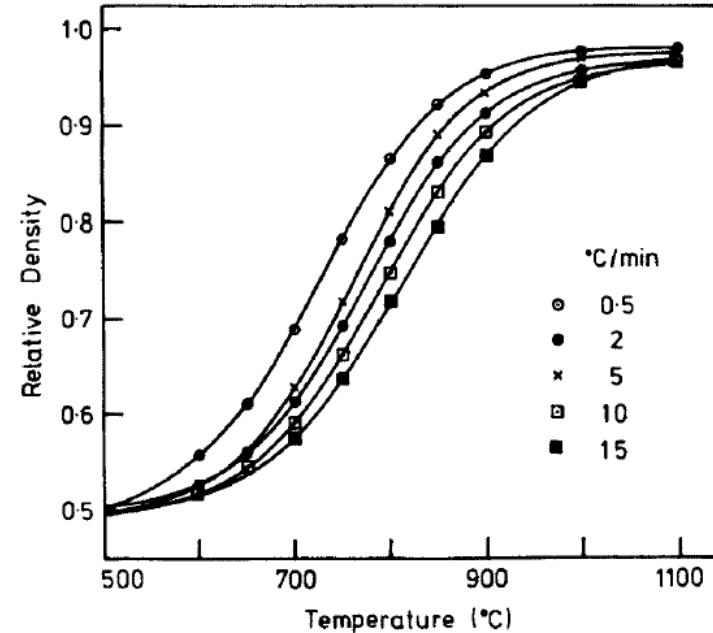


FIGURE 12.8 Relative density versus temperature for ZnO powder compacts with the same initial density (0.50 ± 0.01), sintered at constant heating rates of 0.5–15°C/min. (From Ref. 9.)

Generally, higher heating rates lead to a finer grain size ceramic (it should be clear why...). For ZnO sintered at 1100 °C, average grain size decreases of a factor 2 when the heating rate is increased from 0.5 to 5 K min⁻¹

Master sintering curve

* Compare with Sintering 2, Slide 7

An interesting observation is that plotting the $\frac{1}{\rho} \frac{d\rho}{dT}$ against ρ for sintering data collected at constant heating rate (fig. 12.8), all data falls on the same MSC (fig. 12.9).

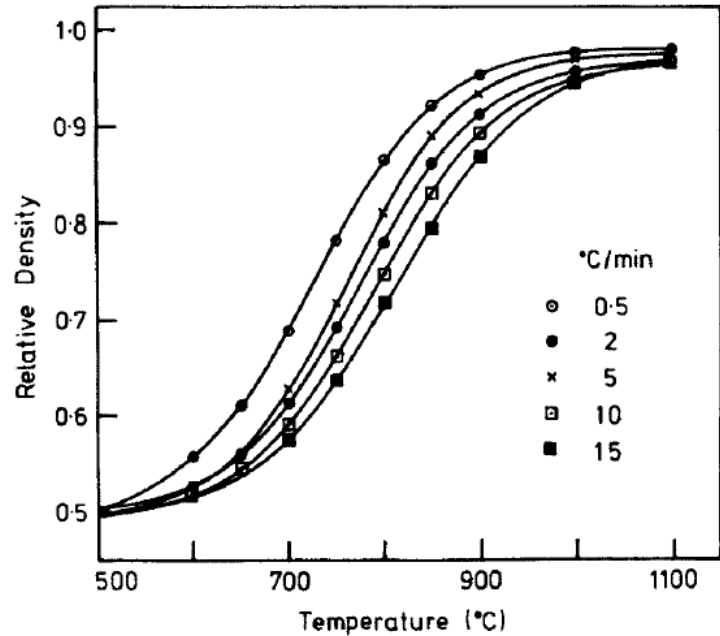


FIGURE 12.8 Relative density versus temperature for ZnO powder compacts with the same initial density (0.50 ± 0.01), sintered at constant heating rates of 0.5–15°C/min. (From Ref. 9.)

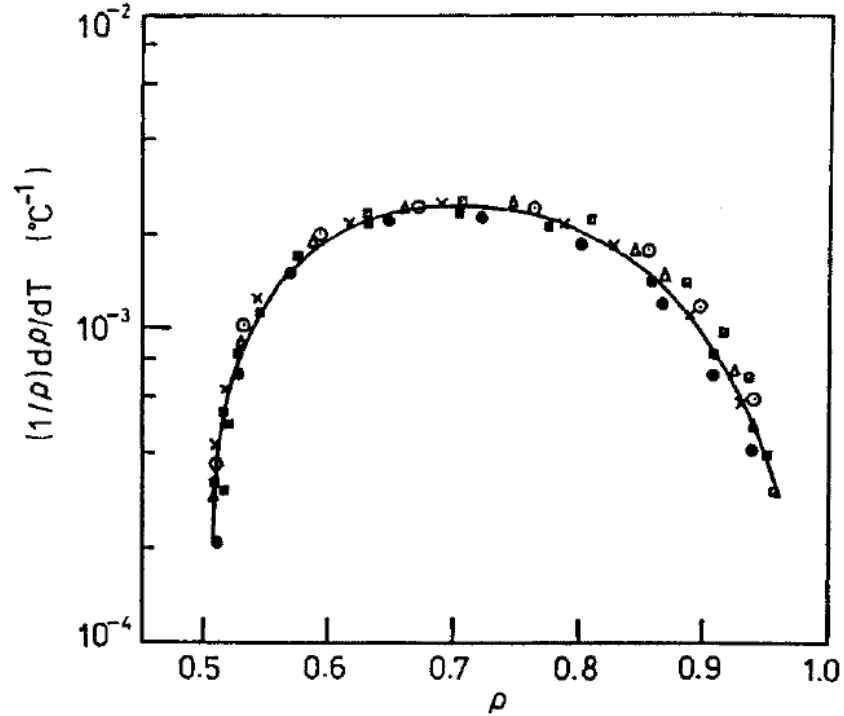
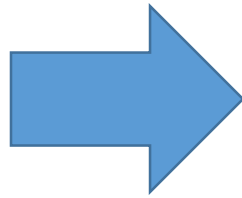


FIGURE 12.9 Change in the densification strain per unit change in temperature as a function of density, determined from the data of Fig. 12.8. The data for the different heating rates fall on the same master curve. (From Ref. 9.)

* Sintering 2, Slide 7

$$\frac{1}{\rho} \frac{d\rho}{dt} = \frac{K(T)}{G^m}$$

t=time; T=temperature

MSC: we keep constant heating rate up to a max T, for the needed time.

Master sintering curve

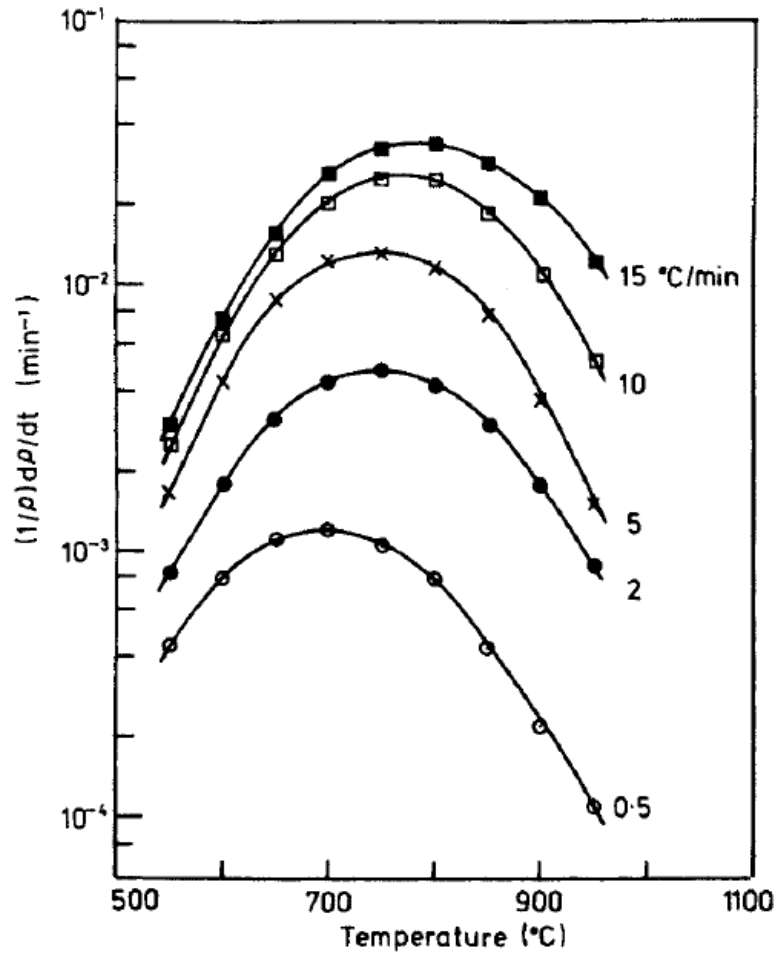


FIGURE 12.10 Densification rate versus temperature determined from the data of Fig. 12.8. Above $\sim 700^\circ\text{C}$, the rate is approximately proportional to the heating rate. (From Ref. 9.)

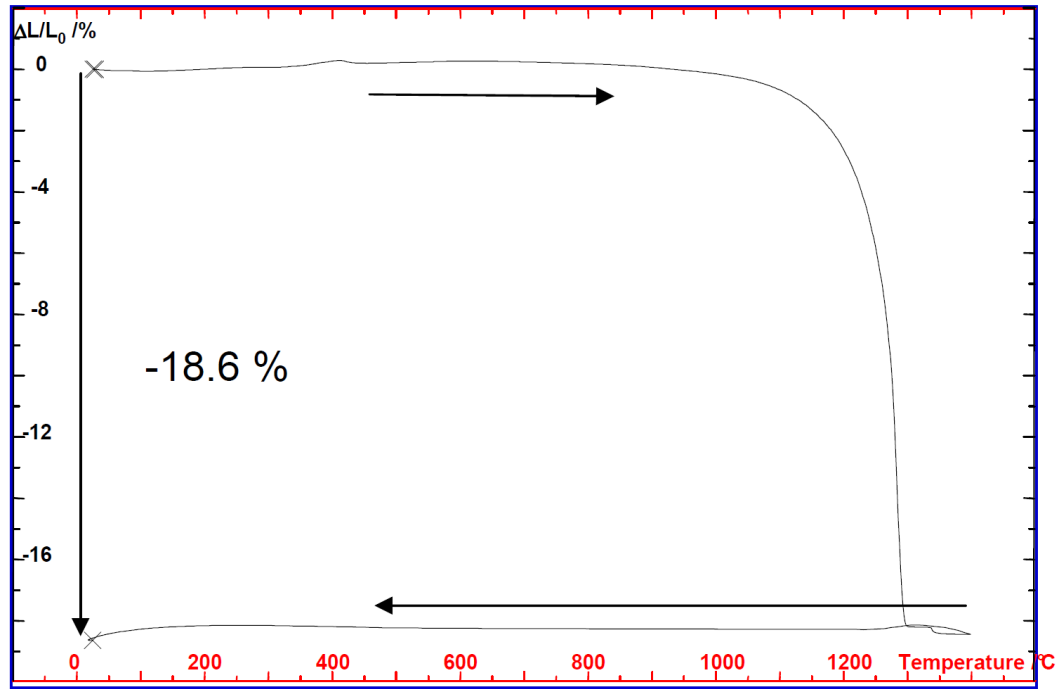
After some mathematics, it can be argue an equation as:

$$F(\rho) = \Theta(T, t)$$

↑
↑
 Densification Thermal history

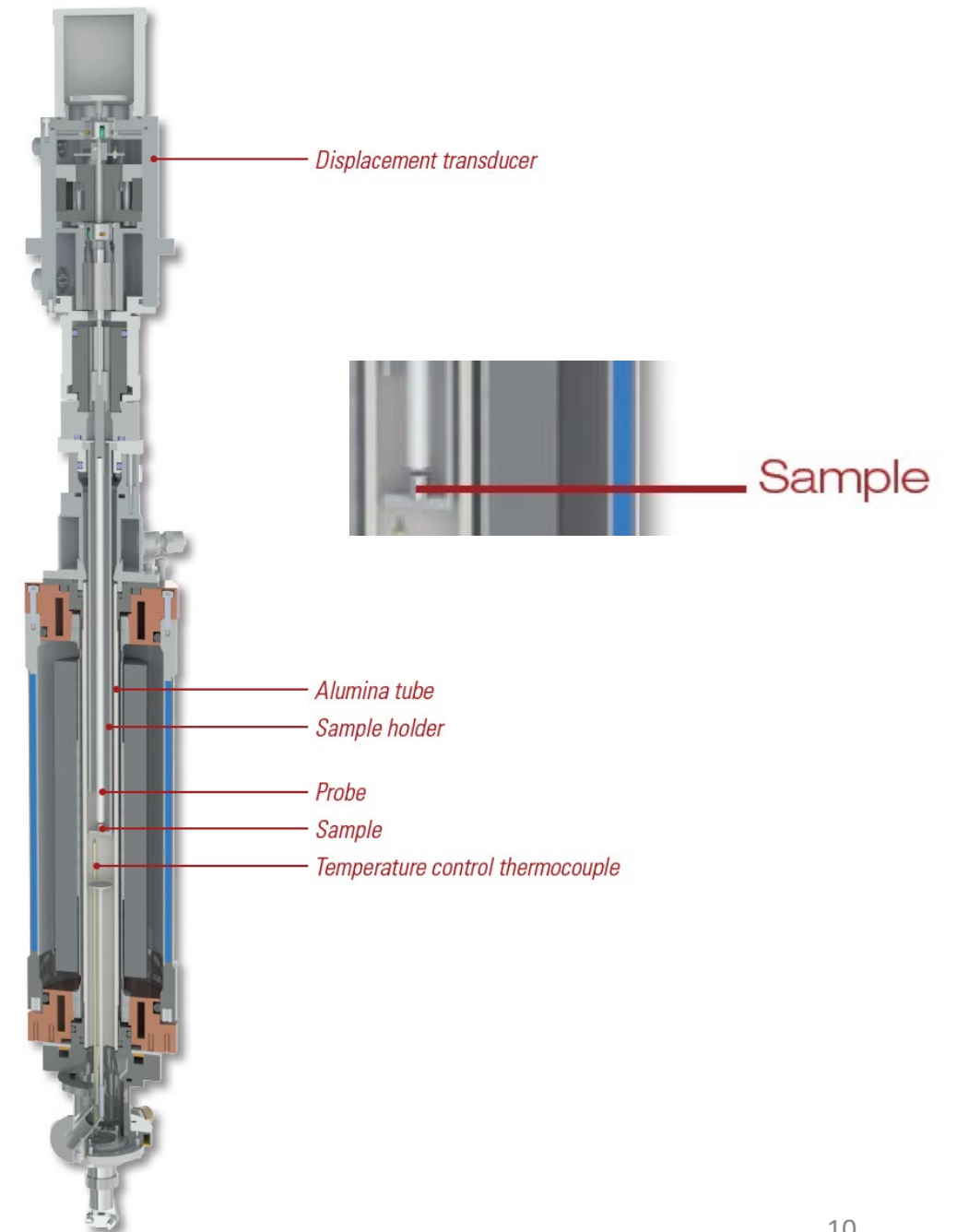
The **master sintering curve** can be constructed from a series of sintering experiments for different times or temperatures. The most economical method of generating the master sintering curve is to perform constant heating rate sintering experiments at four or five heating rates using a **dilatometer**.

Thermomechanical analysis (TMA) / Dilatometry



Controlled sintering rate

Properties of a material are improved by maintaining a constant and slow rate of shrinkage during the sintering process. Key parameters are maximum heating rate and sintering rate. The heating rate can be automatically lowered to follow predefined sintering rate and reincreased at the end of the process. This mode is used to generate an optimized temperature profile and to simulate the sintering process.



Co-firing

It is a process where more than one ceramic is sintered together and a monolithic ceramic is obtained. Co-firing can be: low temperature (< 1000 °C, LTCC) and high temperature (up to 1600, °C, HTCC).

With this technology ceramic microelectronic devices composed by conductive, resistive, and dielectric materials are fired (sintered) in a single process. As a result, a robust multilayered devices is obtained. Initially developed for military application, LTCC are now largely used in the automotive industry and TC.

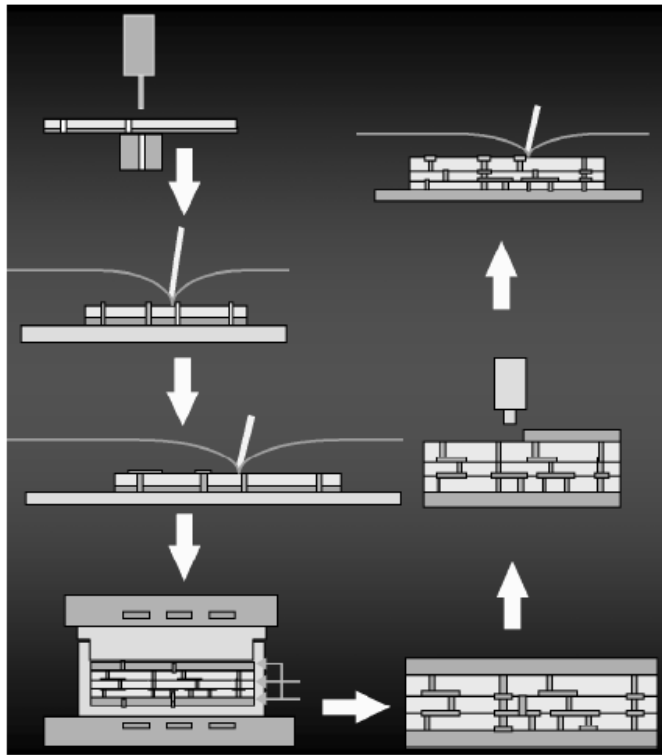


Fig. 1. Process Flow for Non Shrinkage LTCC Production

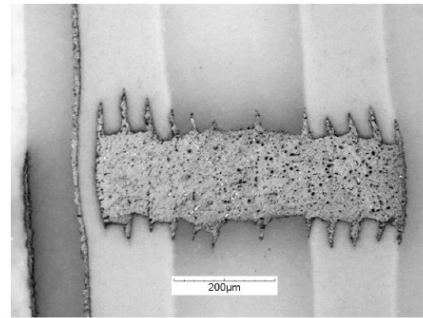


Fig. 2. Stacked via within different layers of ceramic materials

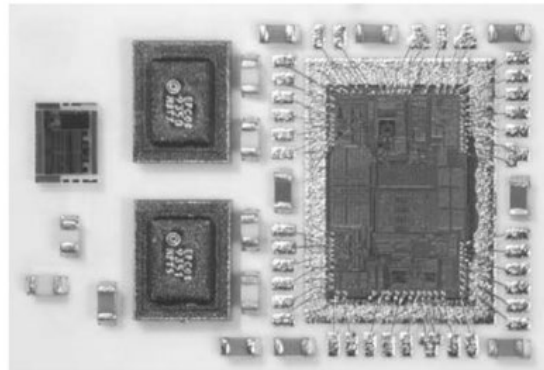


Fig. 7. QB-FEM-TRX-Module Quadriband/frontend mod./transreceiver

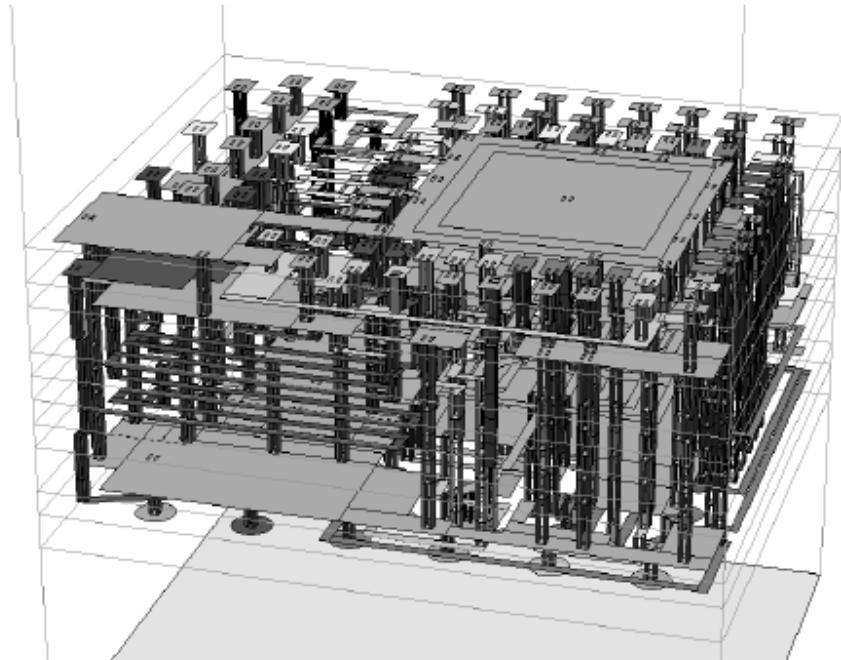
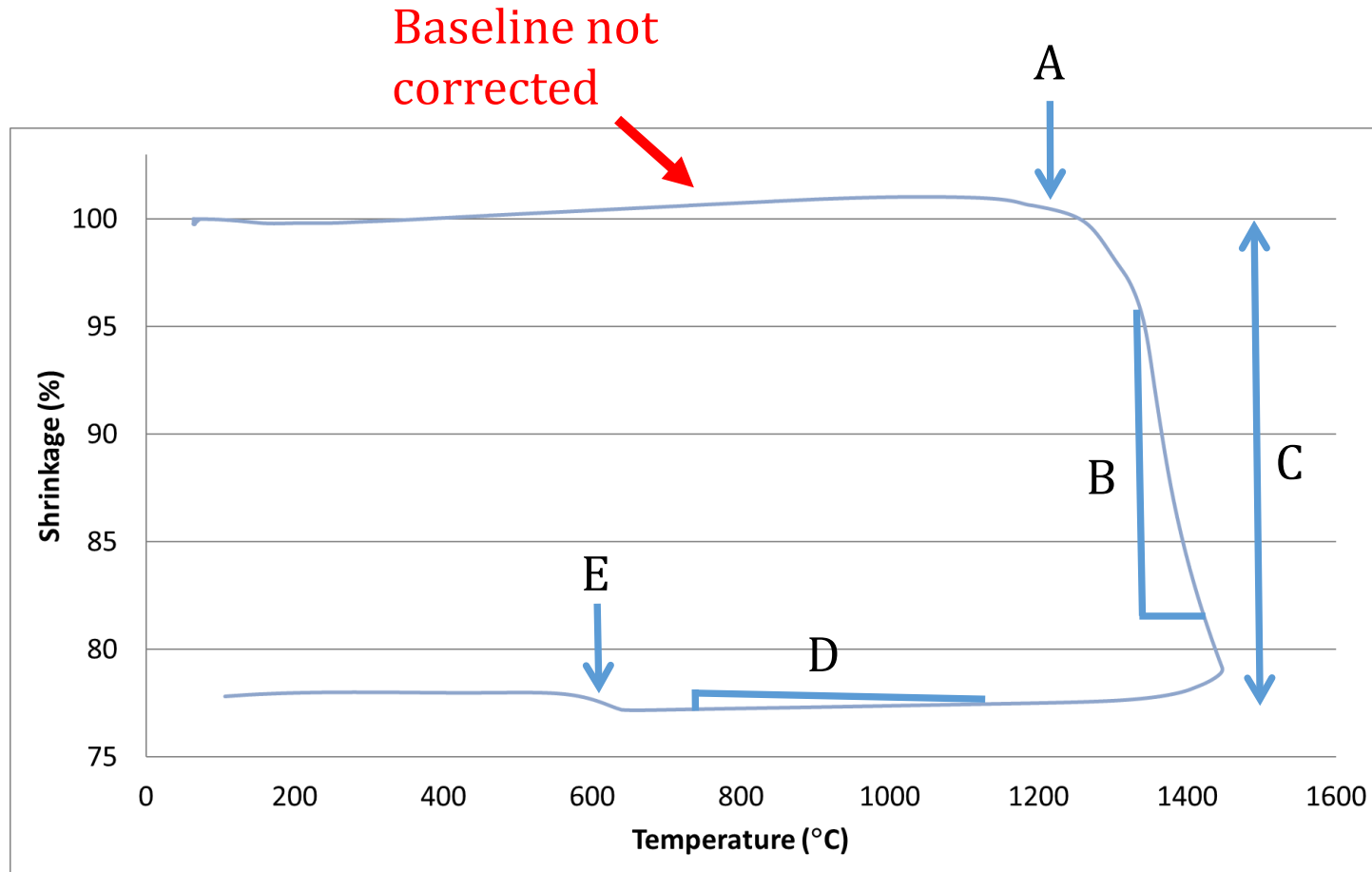


Fig. 6. Scheme of a FEM-TRX-LTCC Module

LTCC Technology for System in Package Solutions
Christian Block, Peter Hagn, Christian Hoffmann, Christian Korden, and Clemens Ruppel
EPCOS AG, Munich, Anzinger Str. 13, Germany,
EPCOS OHG, Deutschlandsberg, Siemensstr. 43, Austria

Co-firing: key (starting) points



- A: sintering onset
- B: shrinkage speed
- C: overall shrinkage
- D: thermal expansion on cooling
- E: eventually, phase transitions

A...E: parameters have to match between materials to be co-fired.
No match → cracks, delamination, failure

Co-firing example: 5 layers active component

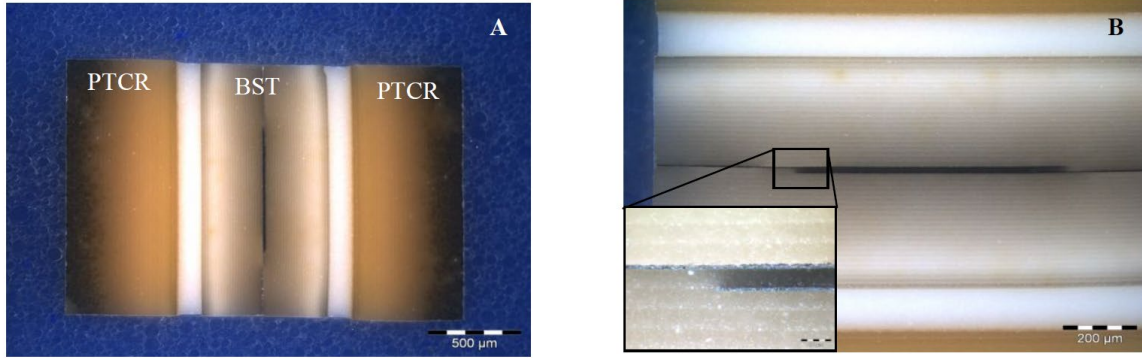
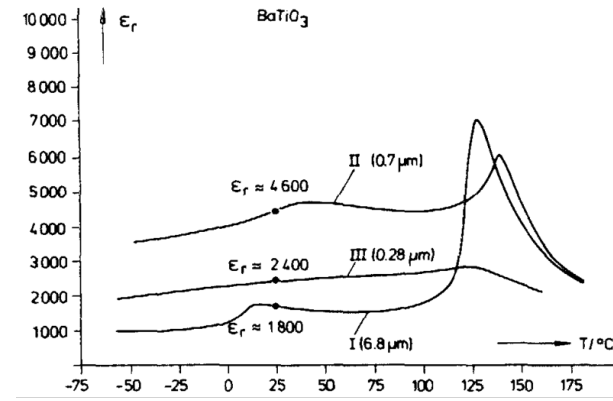


Figure 3 – Device cross sections: (A) overall view, (B) magnification of the inner electrodes' area.



Dielectric constant vs. temperature of BaTiO₃ ceramic showing various grain sizes

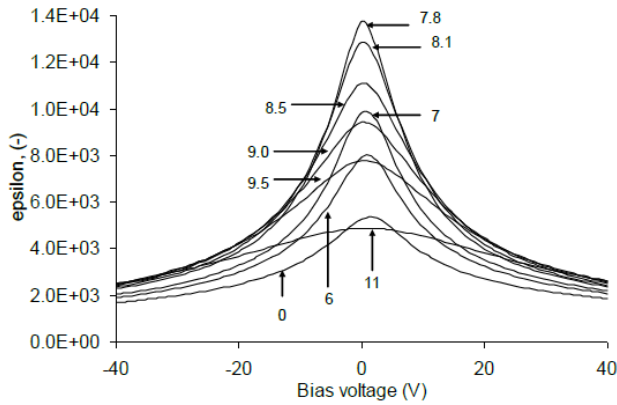


Figure 5 – Dielectric permittivity against Bias_V at different PTC_V (Frequency 200 KHz)

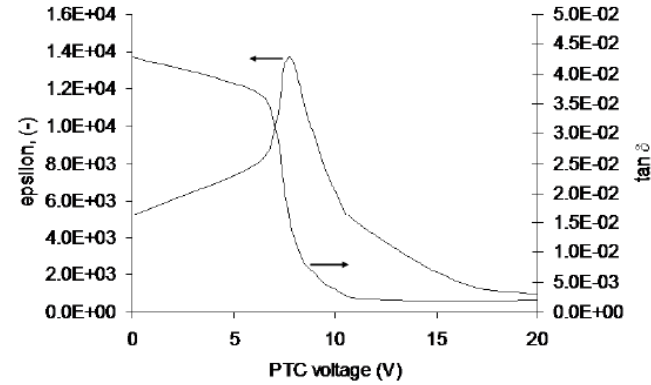


Figure 4 – Dielectric permittivity and dielectric loss against the PTC_V (Frequency 200 KHz)

High Performance Varactor
Andrea Testino

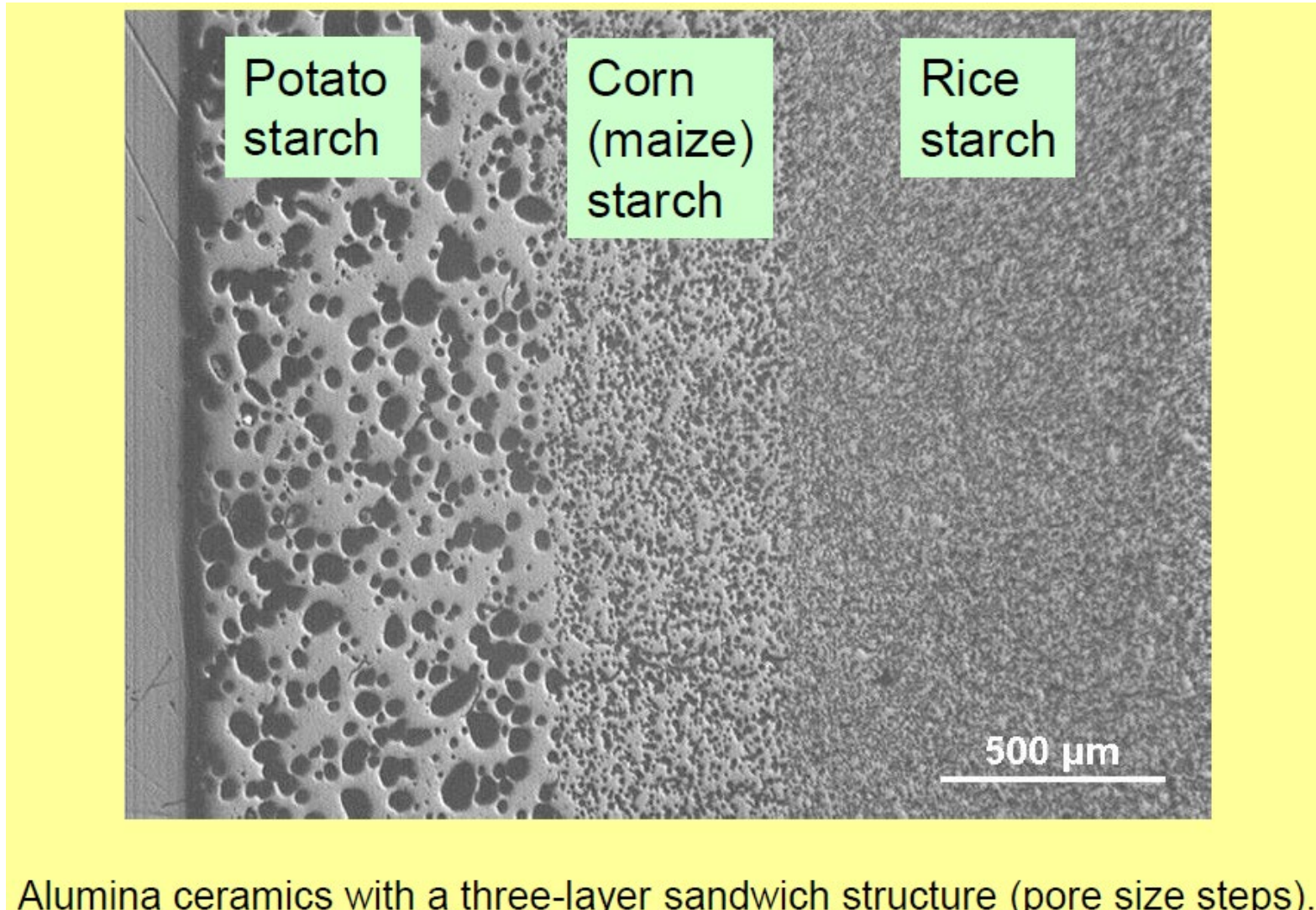
US Patent No.: US 8,988,849 B2
Date of Patent: Mar. 24, 2015

United States Patent
Testino

(2) VARACTOR AND METHOD FOR PRODUCING A VARACTOR
USPC 361/277, 278, 28

TDK-EPC, Corporate Material R&D – Innovative Themes, Deutschlandsberg, Austria
andrea.testino@epcos.com

Pore formers



For some applications, pores are required. Organic pore formers can be used to control the porosity in the final ceramics.

Thermal profile: examples

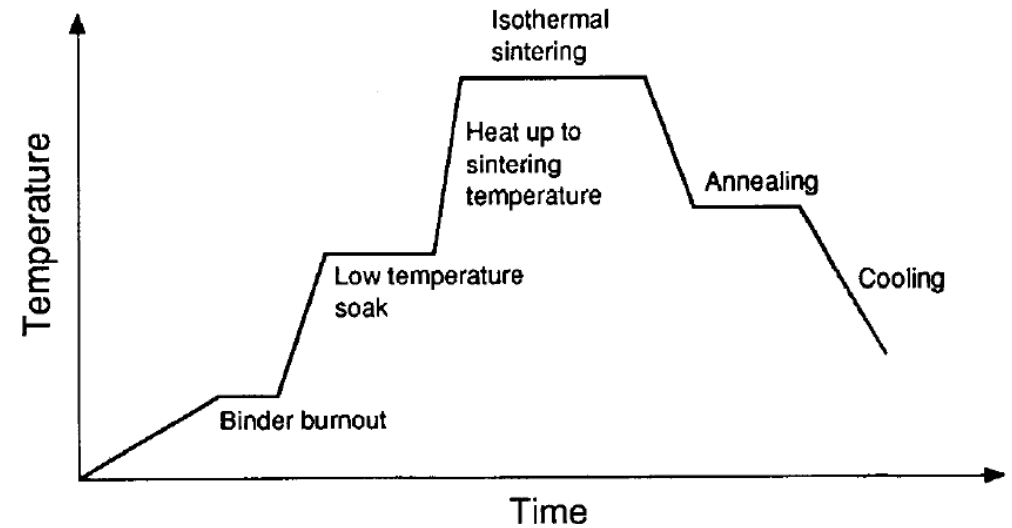
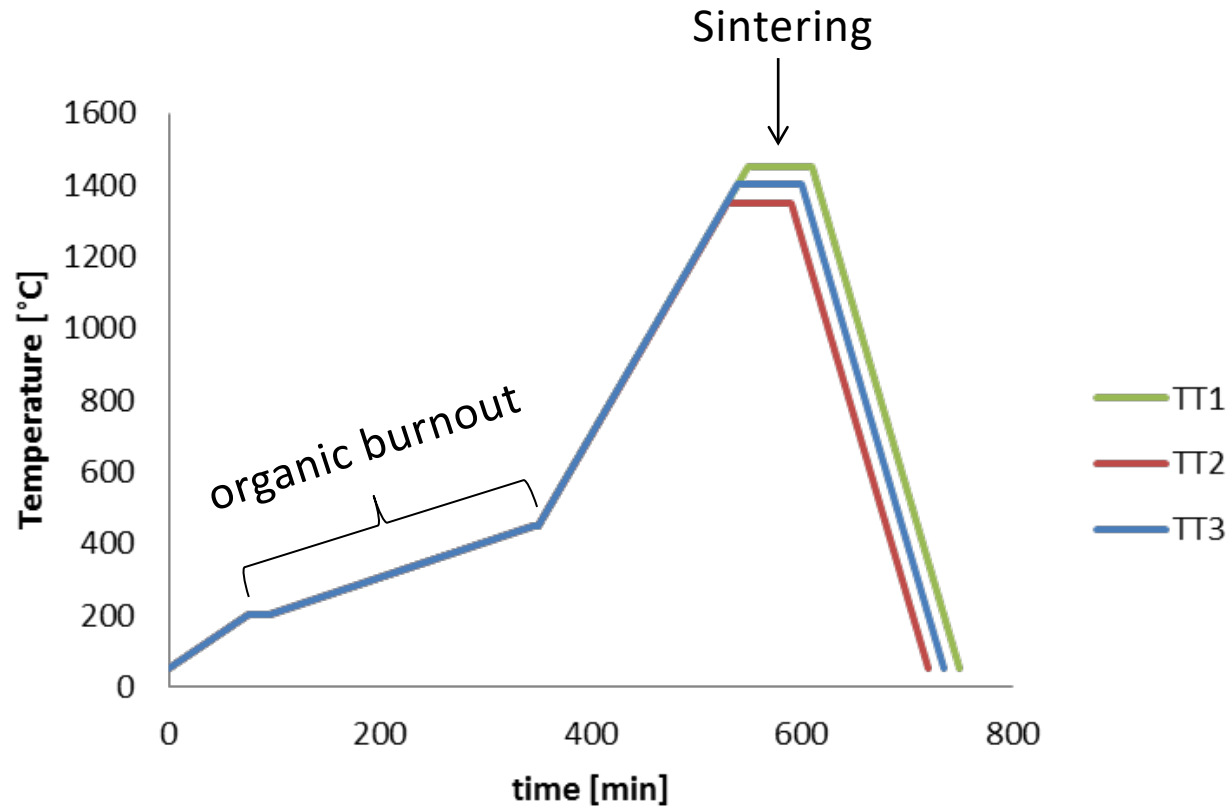
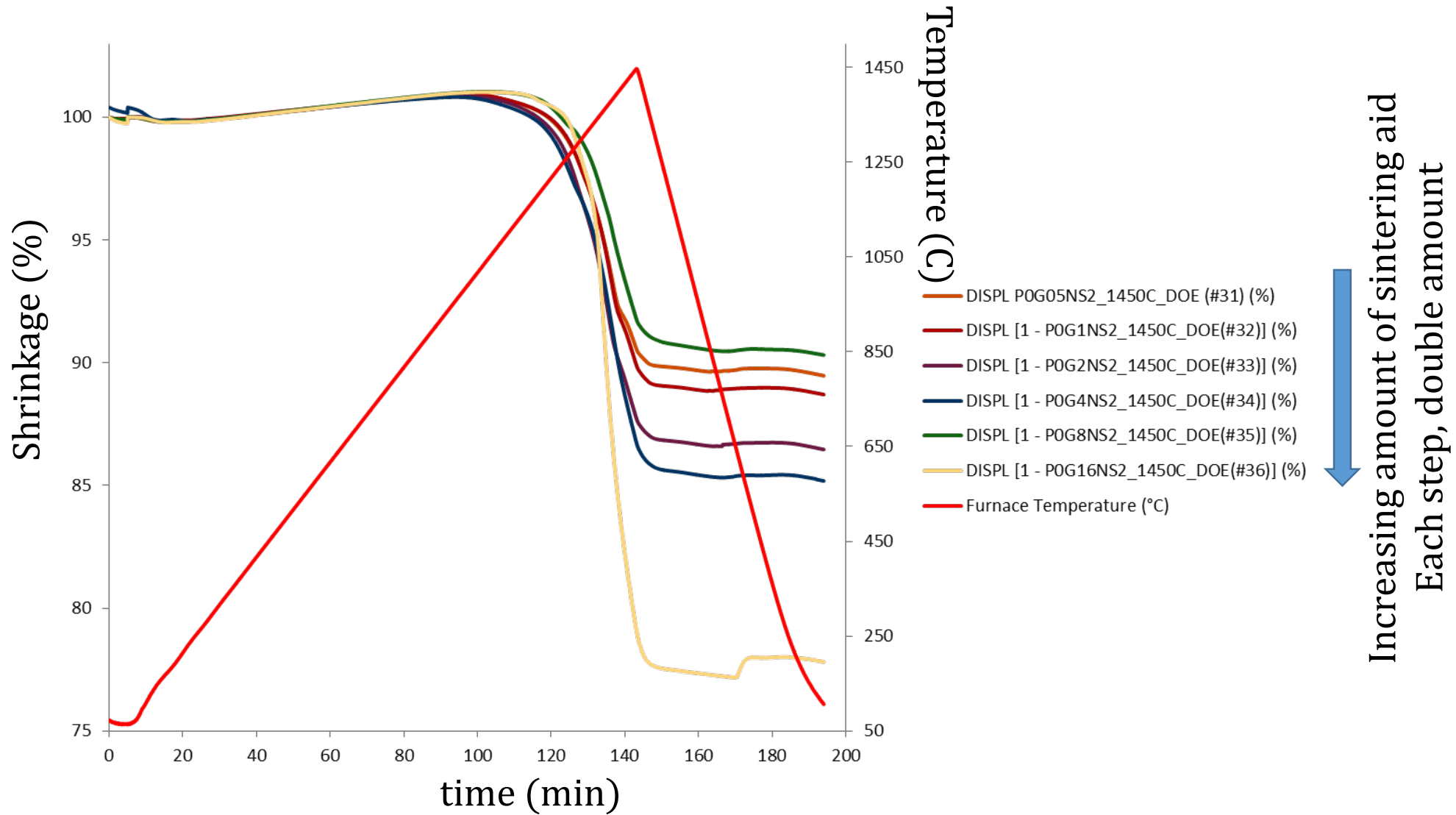


FIGURE 12.4 Sketch of a general heating schedule.

- Initial density (after organic burnout): 0.8 - 1.0 g/mL;
- Sintered body density: 1.3 - 2.5 g/mL

Sintering aids and porous ceramics

Porous hydroxyapatite samples with silica- based sintering aid



Increasing amount of sintering aid
Each step, double amount

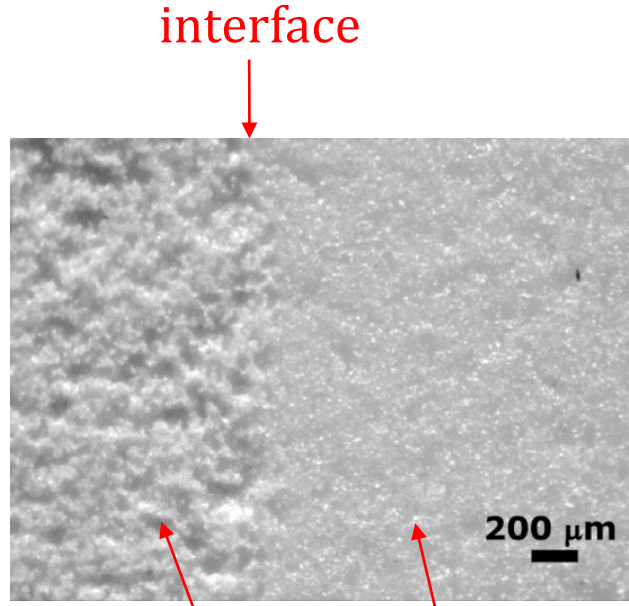
Sintering aids and porous ceramics



Sintering test matrix



Co-fired sample (sandwich A-B-A)



Example of hydroxyapatite co-fired samples with two different porosity and mechanical properties

		Bioglass						
		0.5 wt.%	1.0 wt.%	2.0 wt.%	4.0 wt.%	8.0 wt.%	16.0 wt.%	
Colloidal Silica	0.0 wt.%	CS (MPa)	9	15	15	23	14	--
		d (g cm ⁻³)	1.42	1.49	1.56	1.69	1.57	1.33
	0.5 wt.%	CS (MPa)	41	33	31	23	12	4
		d (g cm ⁻³)	1.71	1.68	1.67	1.59	1.49	1.51
	1.0 wt.%	CS (MPa)	33	29	37	37	4	--
		d (g cm ⁻³)	1.73	1.61	1.68	1.67	1.38	1.49
	2.0 wt.%	CS (MPa)	42	37	32	21	10	--
		d (g cm ⁻³)	1.75	1.65	1.69	1.59	1.45	1.61
	4.0 wt.%	CS (MPa)	38	39	9	48	70	--
		d (g cm ⁻³)	1.60	1.94	1.53	1.81	1.76	2.07
	8.0 wt.%	CS (MPa)	88	91	93	78	33	6
		d (g cm ⁻³)	2.37	2.52	2.53	2.47	2.26	2.23
16.0 wt.%	CS (MPa)	78	77	89	75	39	24	
	d (g cm ⁻³)	2.35	2.48	2.63	2.27	2.09	2.23	

CS: Compressive strength

Practical aspects –Ovens-Furnaces

- Kiln is more widely used in traditional ceramic industry
- Oven is more often for drying ceramics or small furnaces



Combustion Furnaces



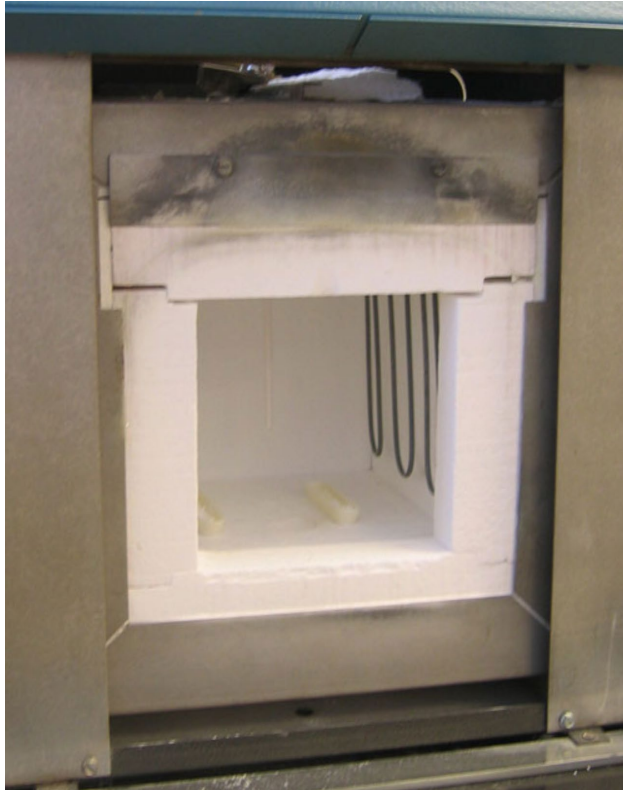
- Gas-fired is the most common combustion furnace. It is mainly for large industrial applications (glass melting, traditional ceramics)
- For large volume production, combustion furnace is more economically favored.

**TABLE 9.1 Standard Molar Enthalpies of Combustion,
 ΔH_c° (kJ/mol)**

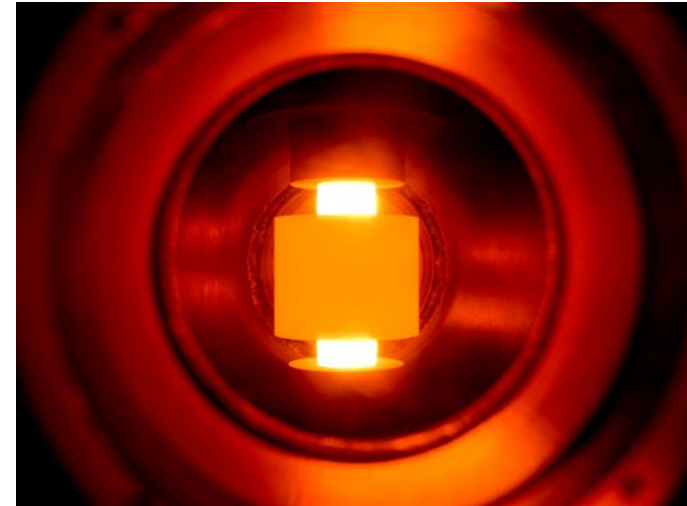
CH ₄ (g)	890
C ₂ H ₂ (g)	1,300
C ₂ H ₄ (g)	1,411
C ₂ H ₆ (g)	1,560
C ₄ H ₁₀ (g)	2,877
C ₆ H ₁₂ (l)	3,920
C ₆ H ₁₄ (l)	4,163
C ₆ H ₆ (l)	3,268
C ₁₀ H ₈ (s)	5,157
CH ₃ OH (l)	726
CH ₃ CHO (g)	1,193
CH ₃ CH ₂ OH (l)	1,368
CH ₃ COOH (l)	874
CH ₃ COOC ₂ H ₅ (l)	2,231
...	...



Electrically heated furnaces



- By thermal radiation
- Typical for small precision parts - dry pressing Ceramaret (Bôle)
- Injection molding - SPT Roth - (Lyss)



By direct Joule heating
(Acheson method of synthesis of SiC)

Indirect Heating Furnaces

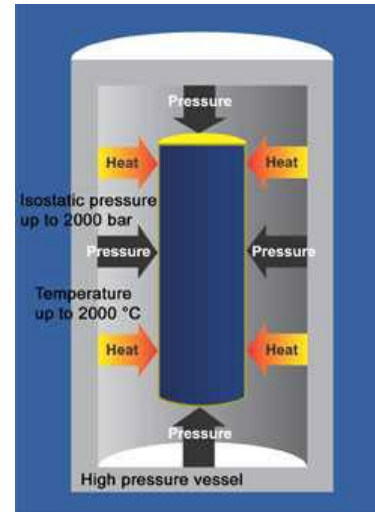
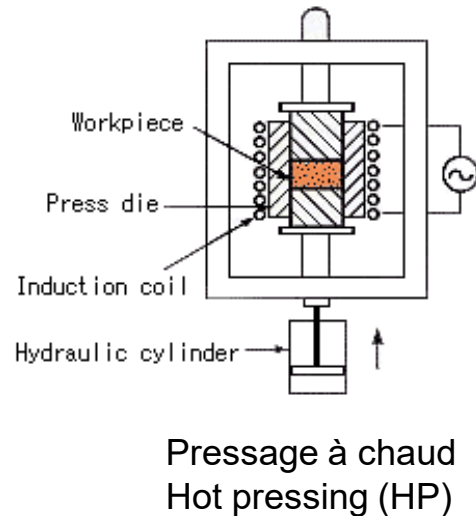


Induction furnaces at 60-1000Hz,
can reach 3000°C.

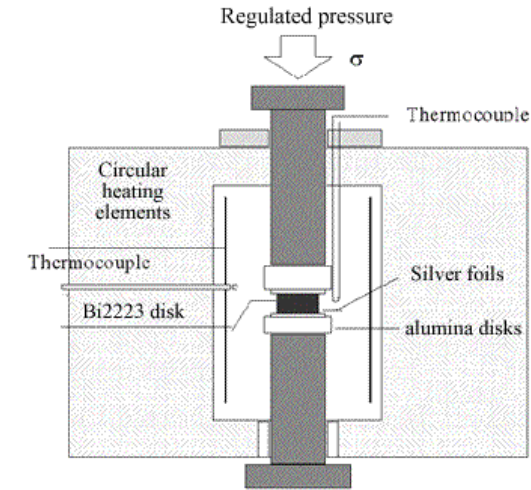


Microwave Sintering is also one kind of induction furnace. Normally working at 2.4GHz for industrial use.

Pressure Assisted Sintering



Hot Isostatic Press (HIP)



Sinter Forging

Advantages:

Improved densification and relatively low sintering temperature (100-500 °C) compared to natural / conventional sintering

Fine microstructure and increased reliability of product properties

Elimination of defects: increased mechanical properties .. up to 3 times!

Disadvantages:

High cost

Carbon contamination in HP

Difficult shape control for forging sintering

Field Assisted Sintering

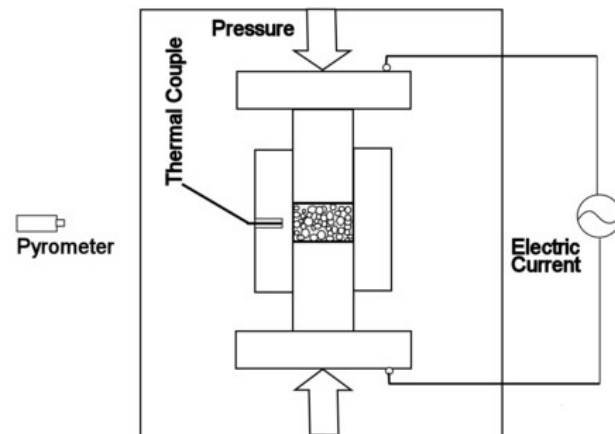
The intrinsic lattice and defect cluster vibration in materials can be coupled with external electromagnetic field and further enhance the mass transport properties. (Theoretical Assumption).

Spark Plasma Sintering (SPS) and Microwave Sintering are so far the most promising and popular sintering techniques in this category.

Up to now, no direct evidence observed in SPS and microwave sintering can support the original design ideas. In SPS still no plasma found and no real pure microwave excitation found in microwave sintering. Need more investigation.

Both sintering techniques have strong advantage in superfast heating and cooling rate, lower sintering temperature and short sintering cycle period.

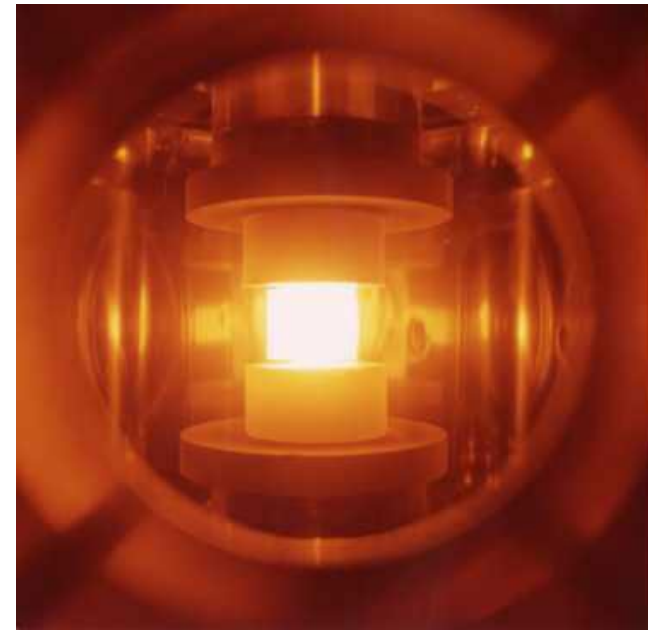
Spark Plasma Sintering



Heat and cooling rate: 10-600°C/min

Maximum Sintering temperature: 2100°C

Pressure: 0-200MPa



Heating by direct resistive heating (Joule effect) with applied pressure!

Finishing - polishing

- A final finishing step is often necessary to ensure the workpiece dimensions or e.g. the sphericity of engine bearings.
- Diamond tools are often needed as ceramics are very hard.
- E.g. ceramic knife video
- <https://www.azom.com/materials-video-details.aspx?VidID=386>
- For ceramics without a glaze or coating there is often a polishing step
- It makes the part more attractive visually and removes surface defects from which a crack can start - this can lead to an improvement of the mechanical properties ... Up to x3!
- Polishing often made with diamond suspensions or pastes



Hip joints