Dipartimento di Ingegneria “Enzo Ferrari”

Microwave assisted sintering of nanostructured metallic powders

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MICROWAVE
APPLICATION
GROUP

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Contents

Aim of the present work is the investigation of the pure microwave sintering of nanostructured AISI 430 powders under applied high electric field intensity, in order to verify if the nanostructure can be preserved and if a satisfactory sample homogeneity can be achieved.

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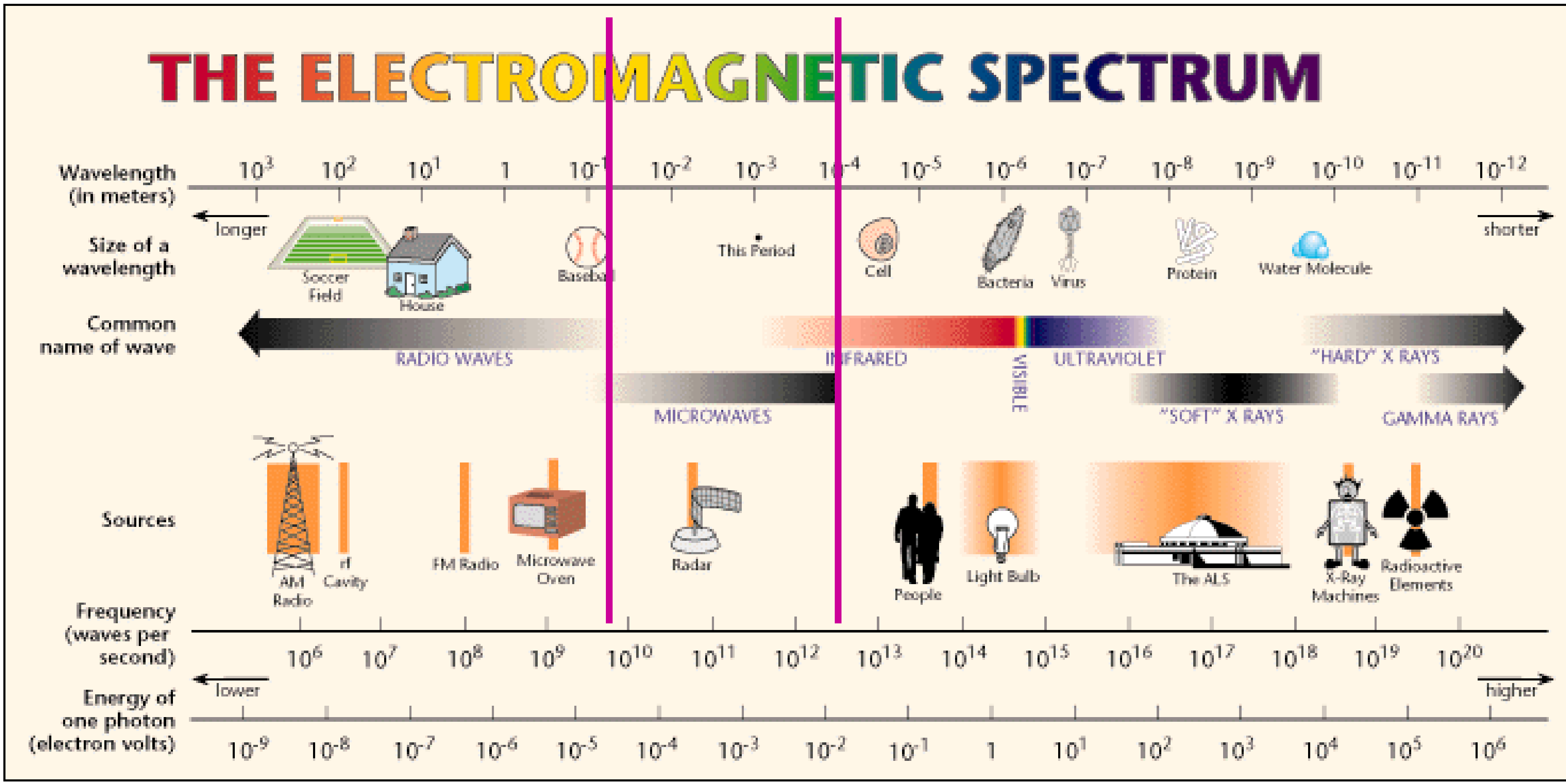
APPLICATION
GROUP

Frequency range: 300 MHz - 300 GHz



ISM Frequencies

(**I**ndustrial, **S**cientific, **M**edical)

FREQUENCY	*DEVIATION*	*AREA*
(MHz)	(+/-)	
433.92	0,2 %	Austria, The Nederlands, Portugal, Switzerland, Germany
896	10 MHz	UK
915	13 MHz	North and South America
2450	50 MHz	Worldwide
3390	0,6%	The Nederlands
5800	75 MHz	Worldwide
24150	125 MHz	Worldwide
40680		UK

Field Assisted Sintering Techniques

- EM field assisted sintering techniques (FAST) :

  minimizing the grain growth [1]

  to obtain, at the same time, *final densities near to the theoretical ones*.

  + a series of phenomena (electromigration, local increase of the diffusion coefficient, action of ponderomotive forces).

- SPS (Spark Plasma Sintering [2]) AND **microwave assisted sintering**

  strong experimental evidence of *accelerated densification*,

  lower porosity

  achievement of peculiar microstructures in the final products

However, the nature of the interaction between microwaves and metallic powders is still subject of controversial studies

[1] J.R. Groza, Nanocrystalline powder consolidation methods, in: William Andrew Publishers, NY, 2002, pp. 115–178.
[2] P. Angerer, L. G. Yu, K. A. Khor, and G. Krumpel, Mat. Sci and Engineering A Volume 381, Issues 1-2, 2004, pp. 16-19

Field Assisted Sintering Techniques

The microwave version of FAST :

-Does not necessarily require the physical contact of a die with the green powders to generate heat, thus some of the lacks of homogeneities could be avoided by this technique.

-Nevertheless, even during pressureless microwave sintering, usually powder compacts are supported by refractory materials and are exposed to the furnace ambient (colder), which can alter the temperature distribution in the material [1].

- However, a proper choice of supporting refractory materials and the use of microwave auxiliary absorbers can help reducing thermal gradients, leading to a much more homogenous dense material [2].

[1] G. Poli, R. Sola, P. Veronesi, Materials Science and Engineering: A Volume 441, Issues 1-2, 2006, pp. 149-156
[2] C. Leonelli, P. Veronesi, L. Denti, A. Gatto, L. Iuliano, J.l of Materials Processing Technology, Vol 205, 1-3, 2008, pp. 489-496

Can we use them to control microstructure?

Heating selectivity

Energy (and not heat) transfer

Inversion of temperature profile

Rapid heating

Volumetric heating

Specific effects (?)

Microwave and Metals

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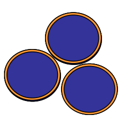
Microwave assisted sintering of metallic powders: paper in 1999 on *Nature* [1]

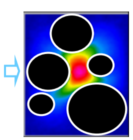
The basic knowledge of the phenomena governing the **interaction between microwaves and metallic powders** is still defective [2] and there are currently three major theories:

$$\delta_s = \sqrt{\frac{2}{\sigma \varpi \mu_0 \mu_r}}$$

Direct absorption of microwaves within the **skin depth** of the metallic material [3], similarly to what happens in induction heating.



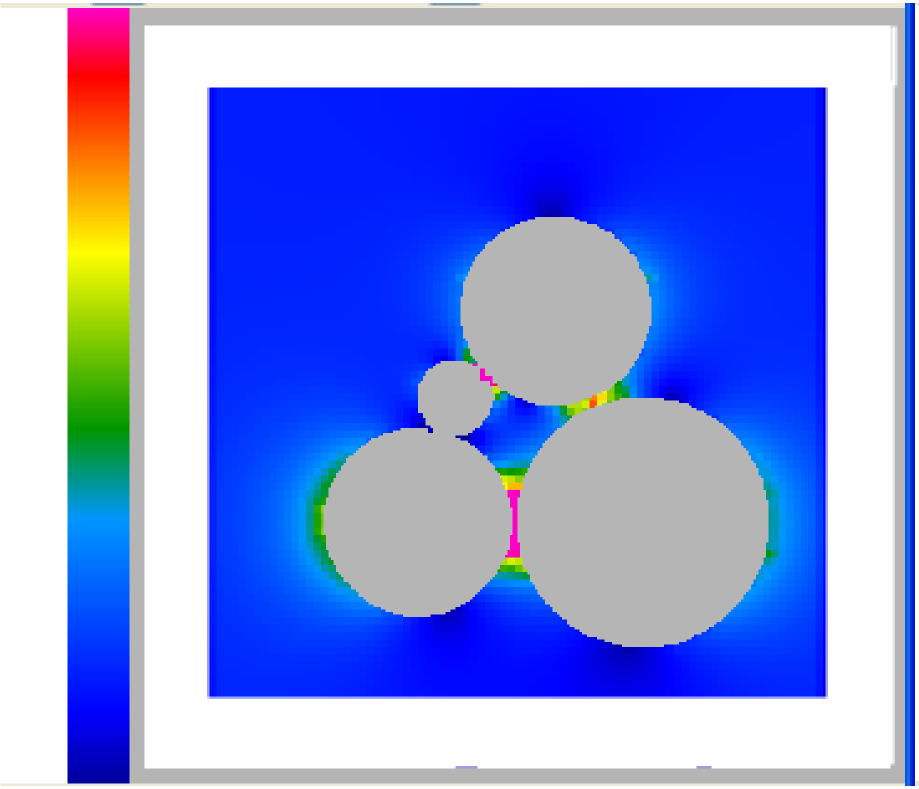
Dielectric heating of the **oxide layer** covering the metal particle [4], which could justify why microwaves penetrate into metal powder compacts to an extent larger than expected

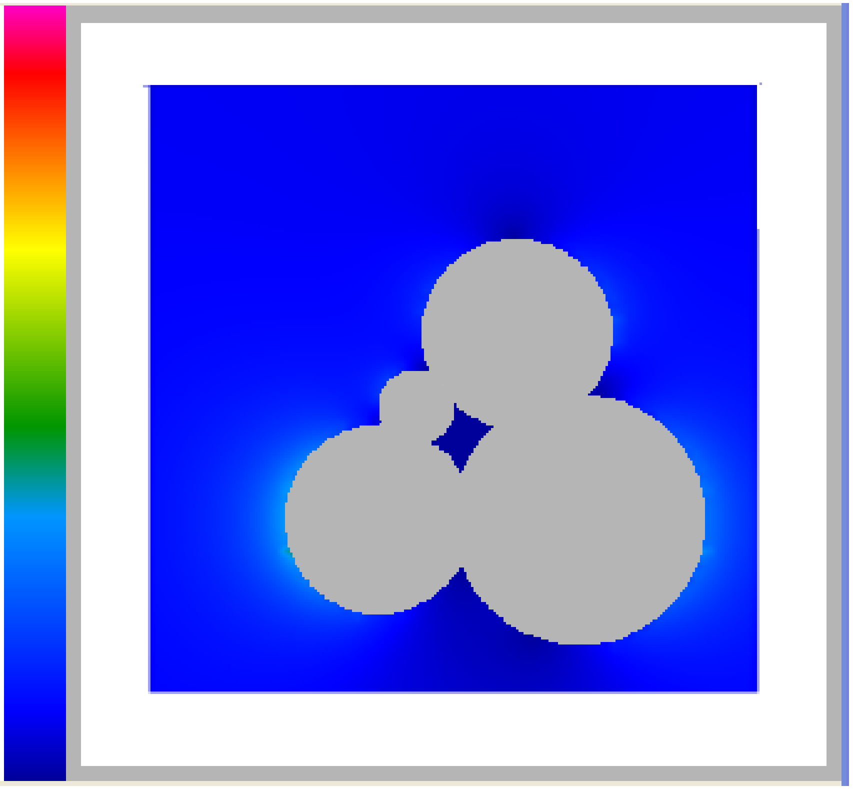


Triggering of **breakdown phenomena** (plasma, electric arcs between the particles) favored by the intensification of the electric field in the area between the conductive particles [5,6].

[1] R. Roy, D. Agrawal, J. Cheng, S. Gedevanishvili, Full sintering of powdered metal bodies in a microwave field, *Nature* 399, 199, 668-670
[2] M. Gupta, E.W.W. Leong, *Microwave and metals*, Wiley, Singapore, 2007.
[3] H.E. Huey, M.S. Morrow, Microwave interactions in the melting of metals, *Proc. 4th W Cong. on Microwave & RF heating*, 286-293, 2004.
[4] K.I. Rybakov, V.E. Semenov, et Al., Microwave heating of conductive powder materials, *J. Appl. Phys.*, 99, 023506, 2006
[5] G. Veltl, F. Petzoldt, P. Pueschner, Effects of microwaves on sintering process, *Proc PM2004 Congr., Vienna, 2004, EPMA.*
[6] P. Veronesi, C. Leonelli, E. Bassoli, A. Gatto, L. Iuliano, Microwave assisted sintering of SLS green metal parts, *SINTERING 2003, , PA, 2003*

Microwave and Metals

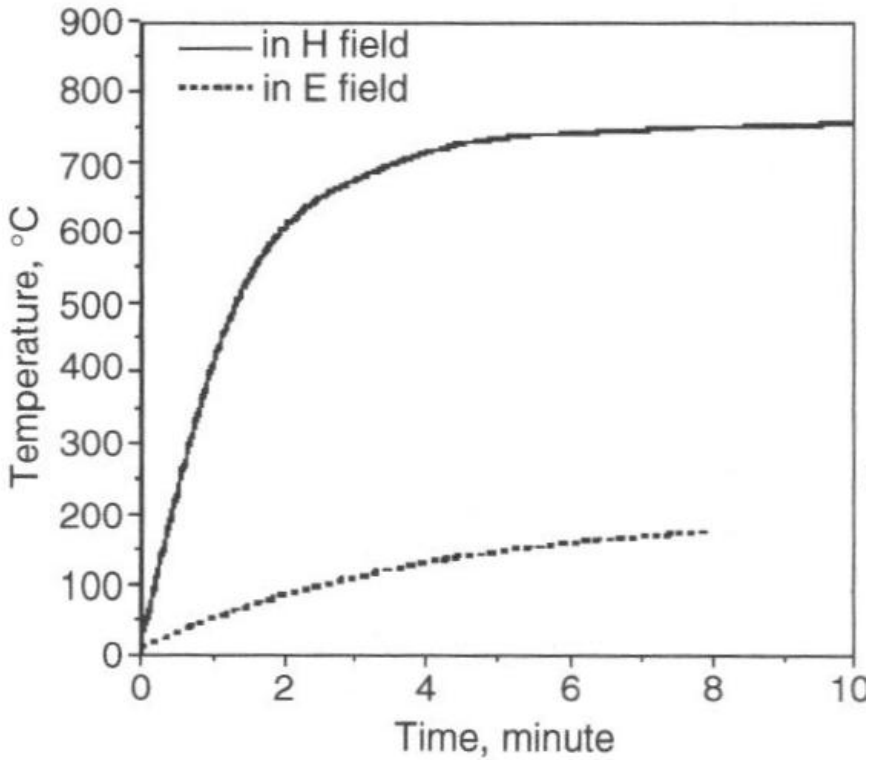




P. Veronesi, C. Leonelli, E. Bassoli, A. Gatto, and L. Iuliano, Microwave assisted sintering of SLS green metal parts, *Proc. SINTERING 2003, Penn State Univ., PA, 14-17 Sept. 2003.*

Microwave and Metals

Different behaviours in **separate E and H field** microwave heating



(i) Steel (Fe+2%Cu+0.8%C)

Cheng, Roy, Agrawal, Mater Res Innov., 5, 2002, 128-140

Materials and Methods

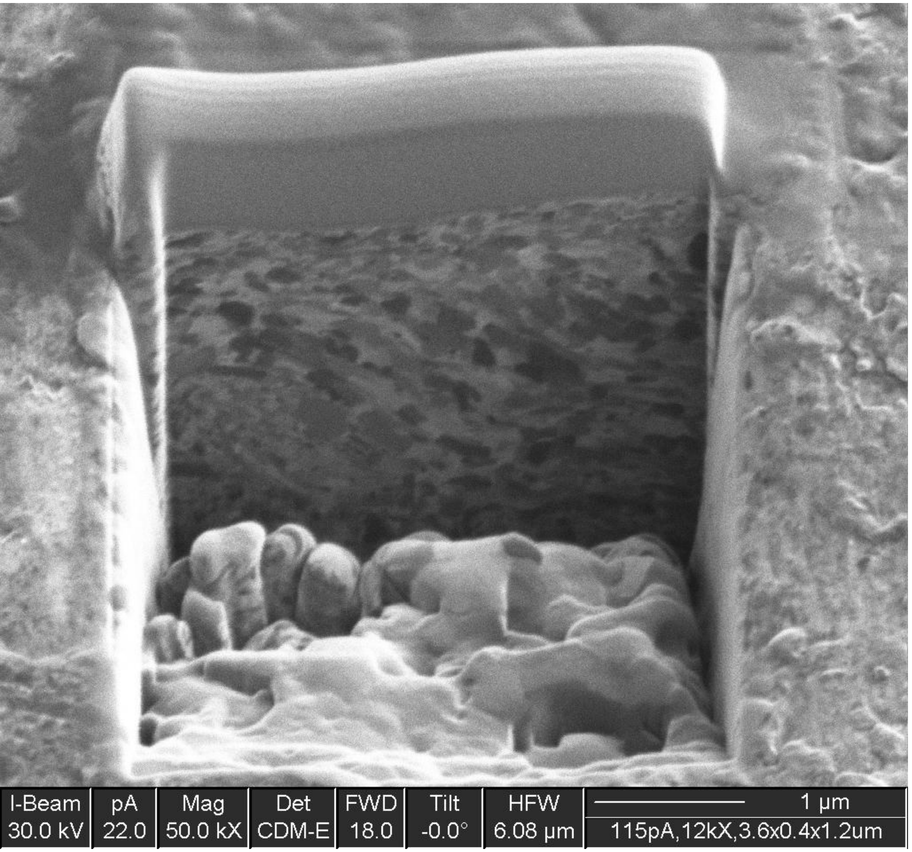
Nanostructured powders of AISI 430 stainless steel (MBN Nanomaterialia SpA, Italy) obtained by a proprietary high energy milling process (Mechanomade®)

Declared average size of the **nanocrystalline domains** is **20nm** (XRD)

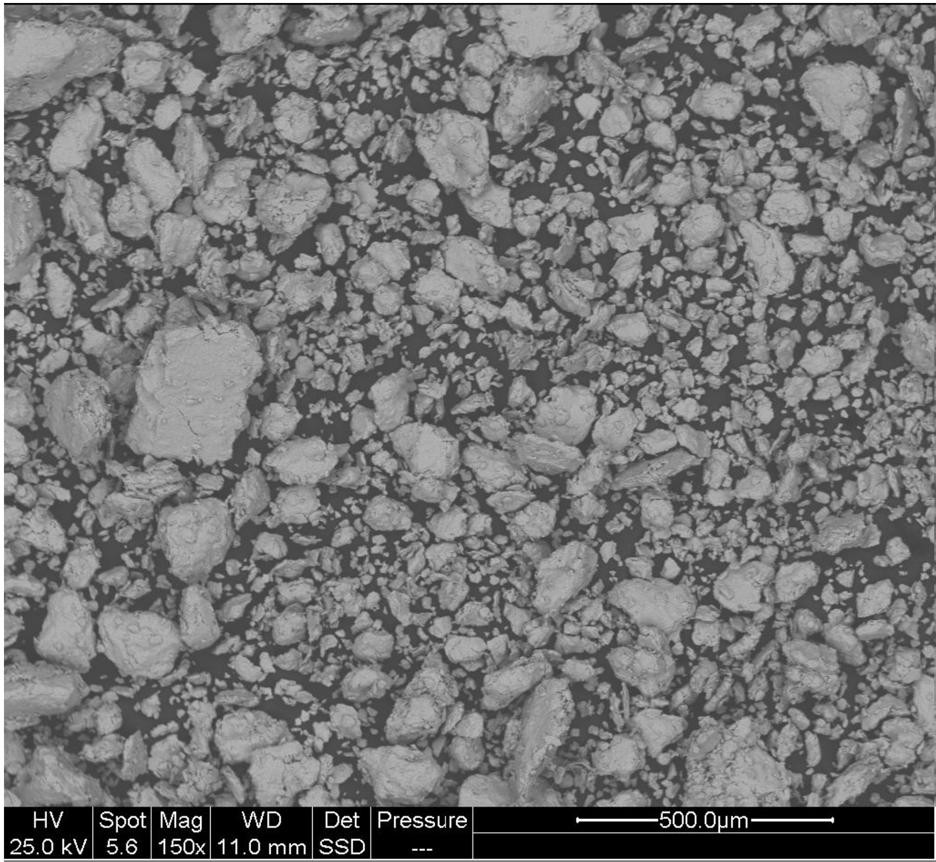
Sieving allowed to select only the powders with **particle size** is **below 250 μm**.

Powders are irregularly shaped, as a result of the high energy milling process

Materials and Methods



FIB micrograph showing nanocrystalline domains in a single particle



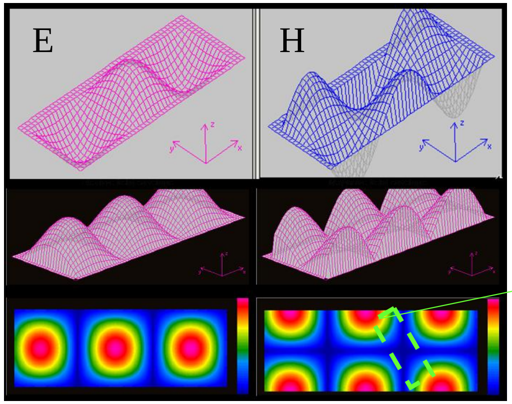
SEM micrograph of the starting nanostructured powders

Materials and Methods

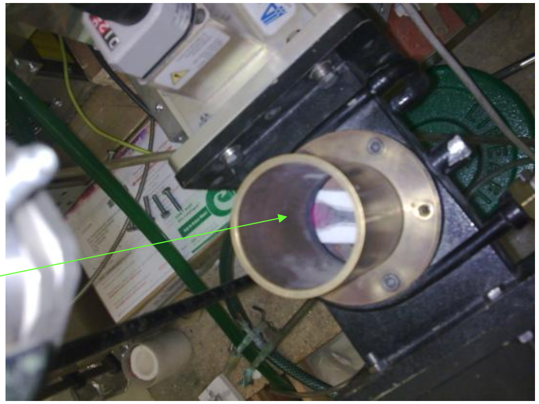
Cylindrical samples (8mm diam, 1 g mass) obtained by uniaxial pressing (550 MPa)

IN

single mode microwave applicator at **2.45 GHz ISM** frequency



Electric (E) and magnetic (H) field distribution and envelope in the single mode applicator (TE_{103} mode); sample position is indicated in green



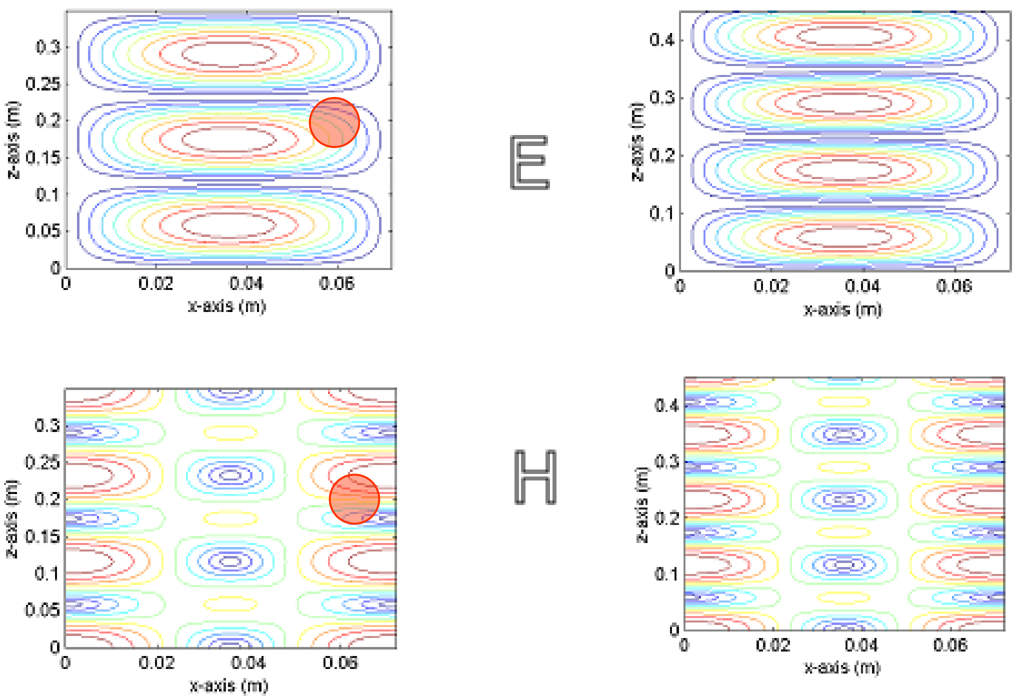
Brown part inserted in the single mode applicator based on the WR340 waveguide, showing preferential heating of the regions placed in maximum H field

Maximum sintering temperature of each sample was varied in the **900-1250C range**, measured by a contact sapphire fibre (Mikron signal conditioner)

Microwave forward power was varied accordingly, in order to achieve sintering in **less than 100s**

The idea

Samples were placed, one per run, in the region intermediate between maximum electric field (E) and maximum magnetic field (H) intensity and subjected to a 20 Nml/min N_2-2%H_2 flux to prevent oxidation.



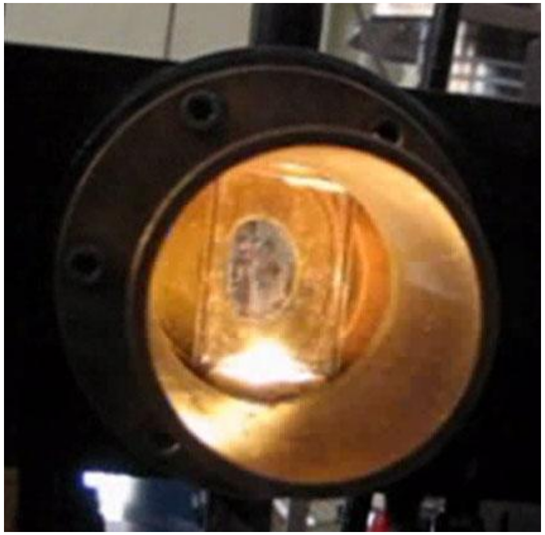
Sample position, intermediate between the two maxima of field intensity, was chosen so that not only direct microwave heating occurs, but also breakdown phenomena triggered by the high electric field can take place between the powders.

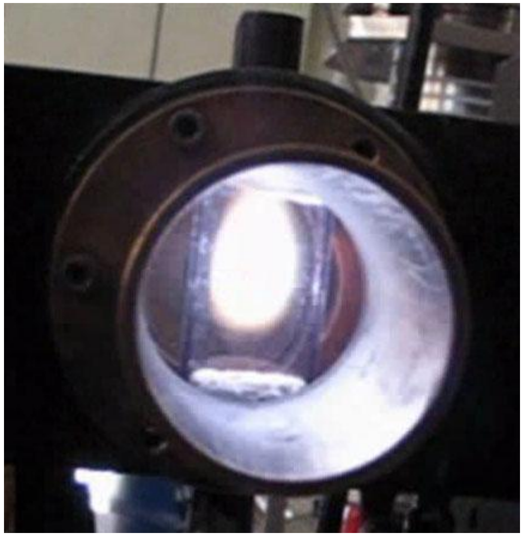
This is expected to lead to early necks formation and overheating limited to the particles surface, in order to try to prevent coarsening

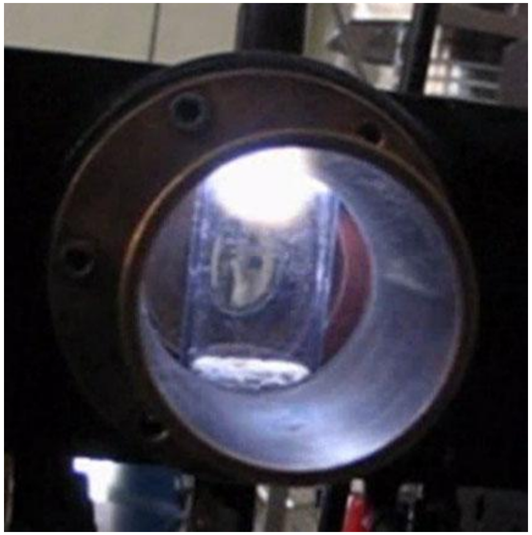
Results

plasma formation

<u>Non optical sensors could be used for top surface temperature masurments !!!</u>







Results

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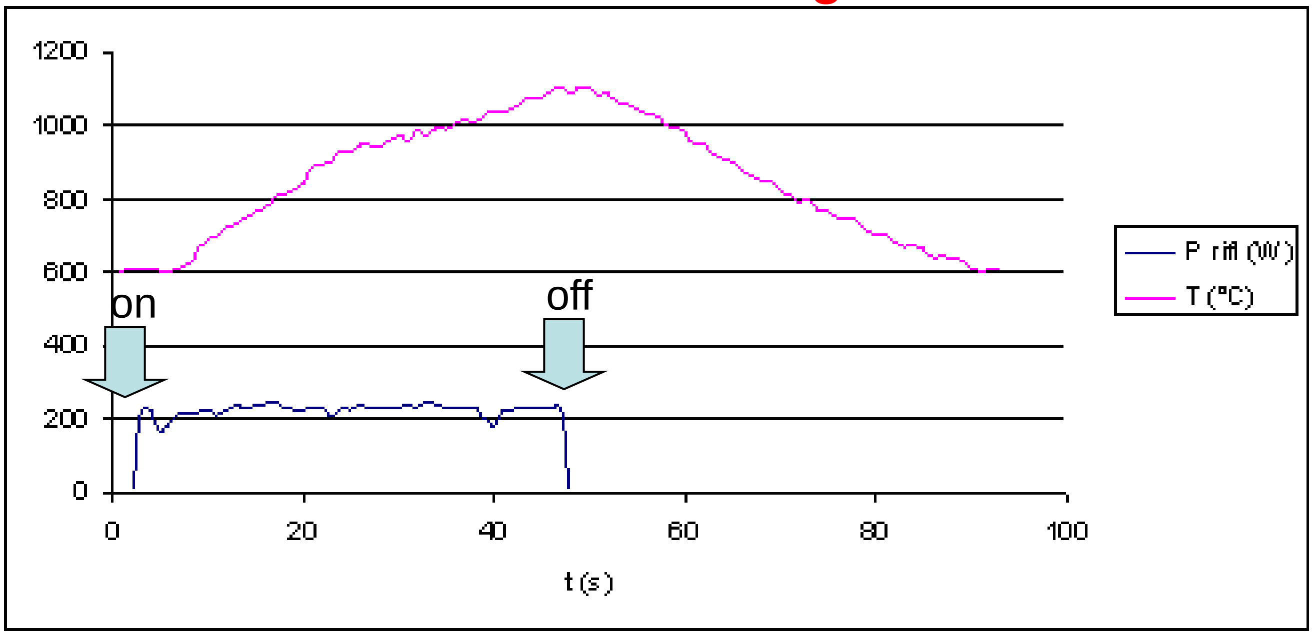
microwave heating curve



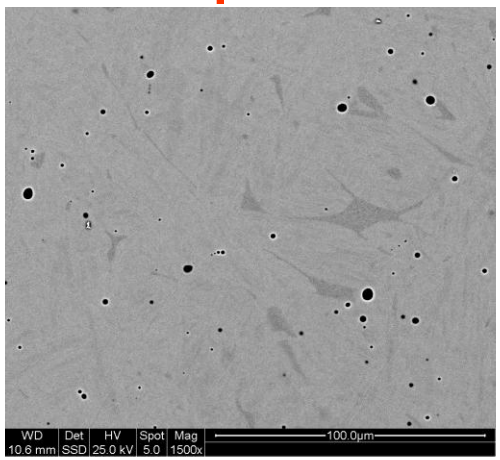
During the first 5 seconds (from time= 3 s to time= 8 s) a temperature increase of almost 600C is experienced by the material, which then starts to heat less rapidly.
A possible explanation could be that the powders reached the **Curie temperature**

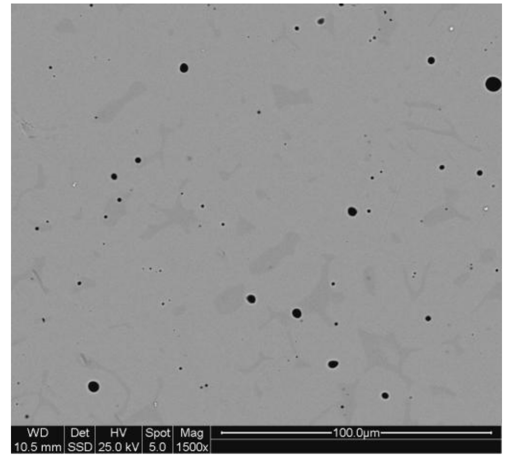
$$P_d(x,y,z) = \omega\, \varepsilon_0 \varepsilon''_{eff} E_{rms}^2 + \omega\, \mu_0 \mu''_{eff} H_{rms}^2$$

Results

separate E and H Field

1150°C, 64 s, 800 W





1200°C, 39 s, 1200 W

SEM micrograph of sintered samples showing residual porosity and -
Cr enriched regions (darker areas)

Porosity of the samples sintered at 1150-1200 C resulted **lower than 1%**

maximum magnetic field: a more controllable and reproducible sintering

maximum of electric field: in arcing between the particles and less reproducible treatments

P. Veronesi, C. Leonelli, and G. Poli, Microwave enhancement of the early stages of sintering of metallic powder compacts and metal-containing composites, *Microwaves in the Engineering and Applied Science*, E. Caponetti, Ed., 2007, 125-138.

Results

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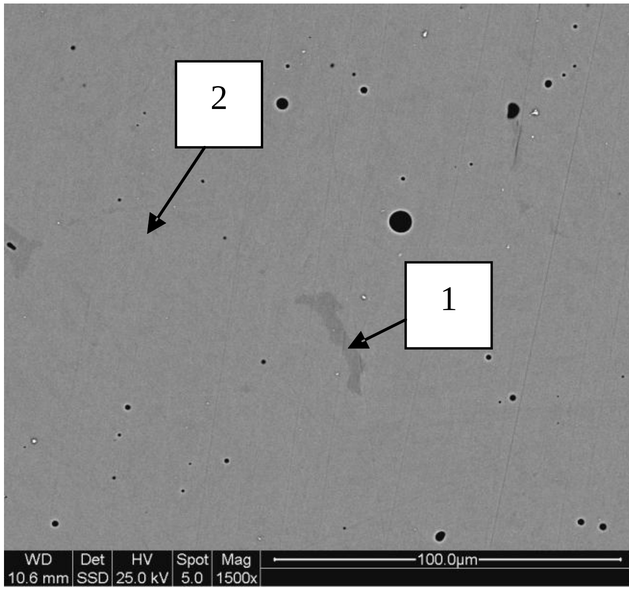
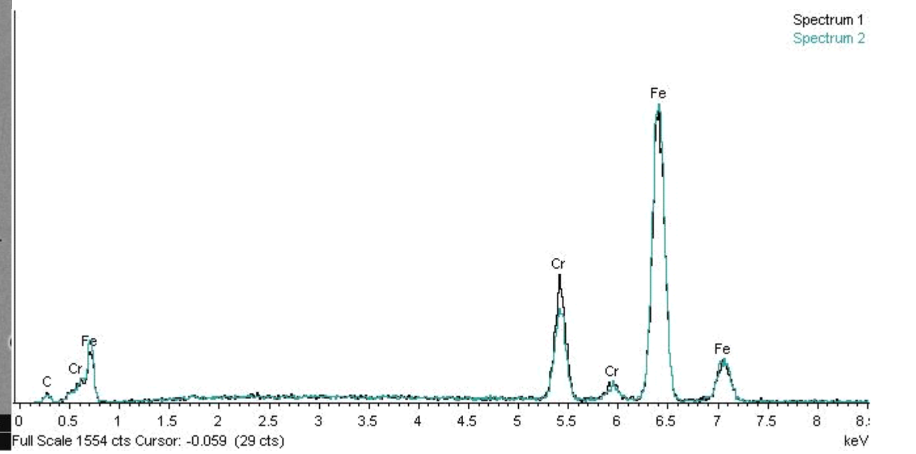
Cr distribution



Spectrum 1: Cr= 16.89%
Spectrum 2: Cr= 15.45%



- **Cr-richer regions**, which correspond roughly to the former particles borders.
- This, and the fact that **no debinding** has been performed on the green parts prior to sintering, despite the use of lubricated die, could be ascribed to the formation of **chromium carbides** at the grain boundaries, where **localised heating** occurred and the lubricant acted as a source of C, leading to a slight **sensitisation** of the stainless steel, as confirmed by previous studies [1].

[1] P. Veronesi, C. Leonelli, L. Denti, A. Gatto, L. Iuliano, Preliminary studies of the rapid microwave sintering of green parts made of 420L stainless steel, EUROPM2006 Proceedings vol2 - powder injection moulding, 2006, pp.183-188

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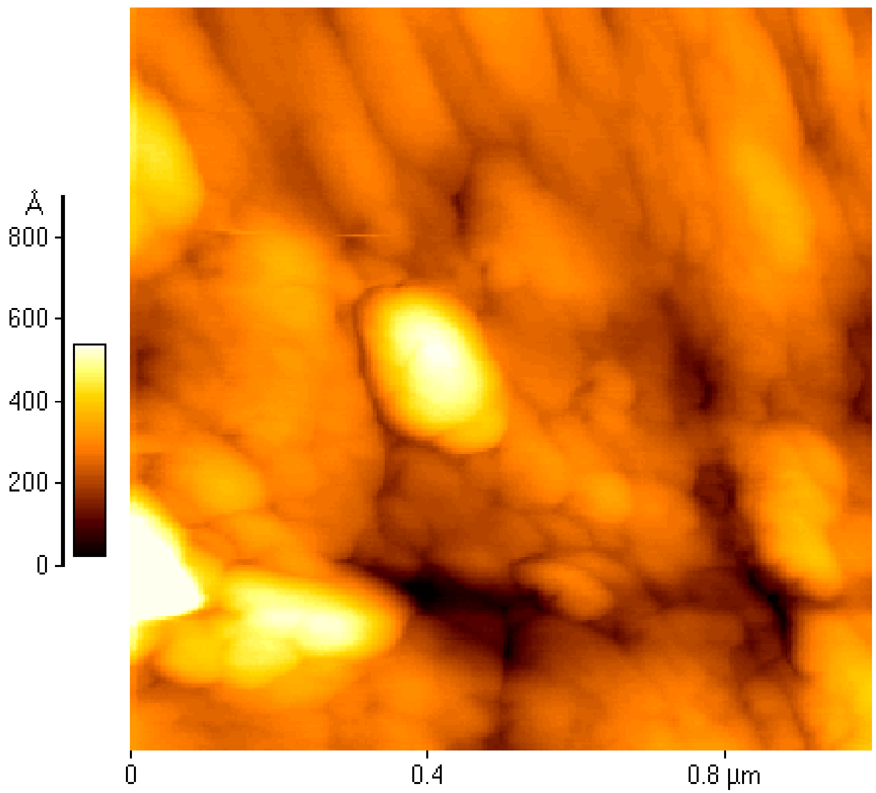
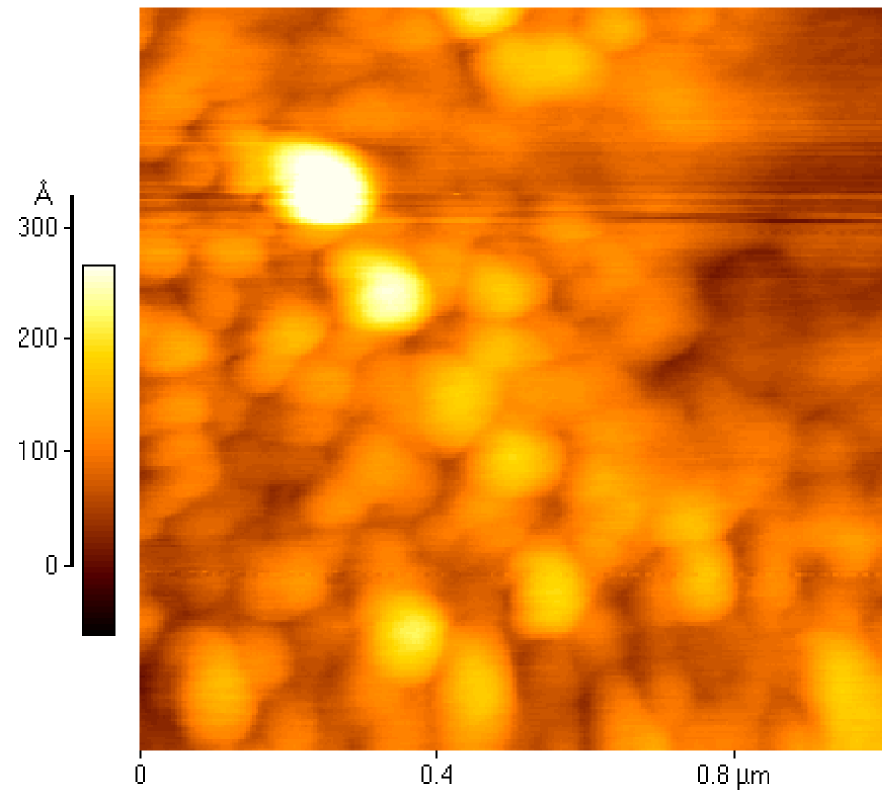
Results

nanostructure and microhardness

Multi Image Presentation



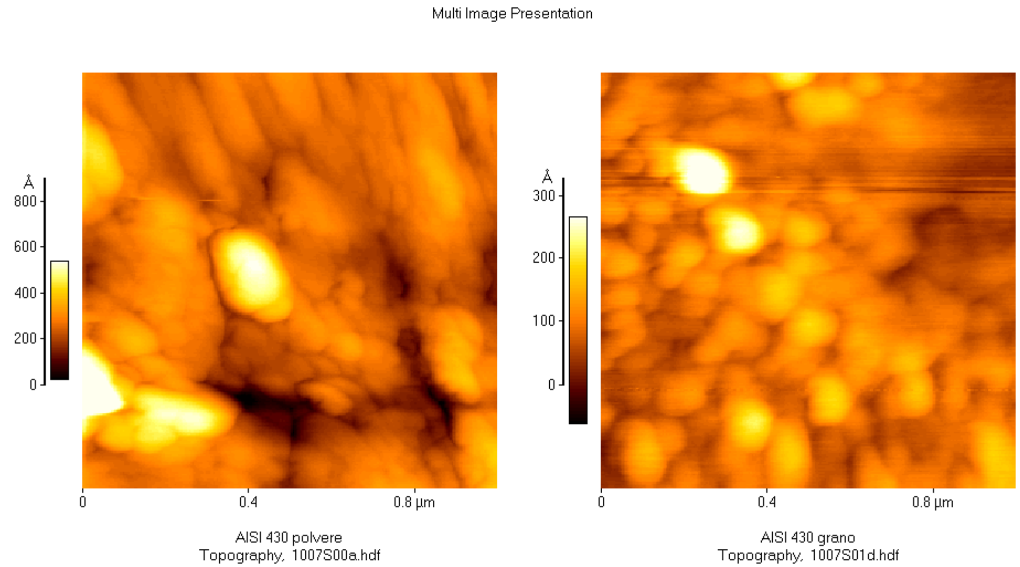
AISI 430 polvere
Topography, 1007S00a.hdf



AISI 430 grano
Topography, 1007S01d.hdf

Results

nanostructure and microhardness



Microwave sintering **lead to nano- or sub-micrometric grains**, despite the non- homogenous densification due to the uneven EM field distribution in the single-mode applicator.

The average measured micro-hardness of the microwave sintered parts @1150C (**520 HV_1**) resulted almost three times higher than reference bulk material hardness (**190 HV_1**), indicating that the expected possible reinforcement by grain size refinement occurred.

P. Veronesi, R. Rosa, C. Leonelli, G. Poli, E. Bassoli, L. Denti, and A. Gatto, Microwave assisted debinding and sintering of nanostructured metal powders: modeling and experimental results, *Workshop on Metamaterials and Special Materials for Materials for Electromagnetic Applications and TLC,, 2008*.

Results

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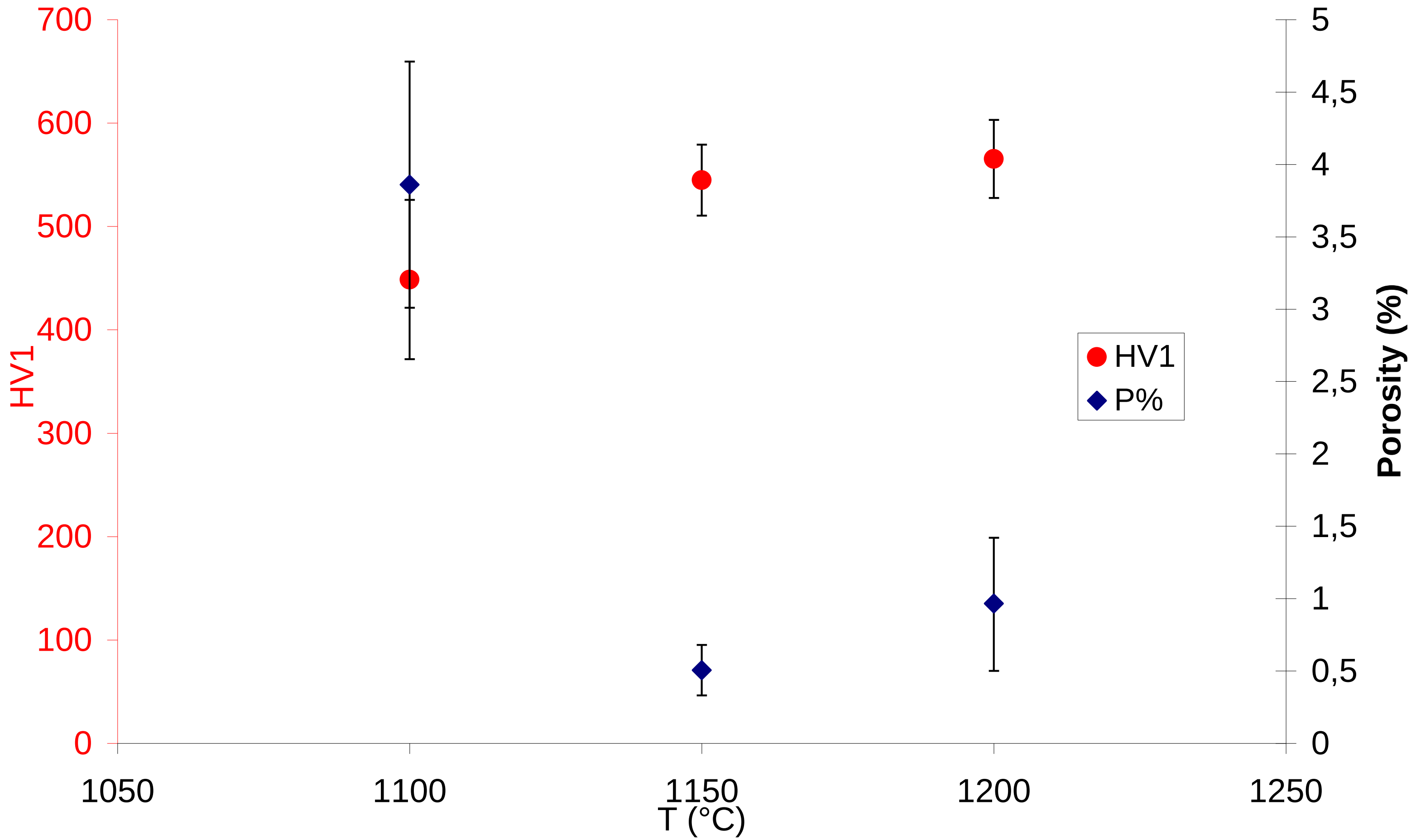
nanostructure and microhardness



Conclusions

- Microwave sintering in single mode applicator allows to **rapidly densify** the samples, leaving a **less than 1% round shaped residual porosity** and partially preserving the **nanostructure** of the starting powders. Moderate grain growth, however, occurred already starting from 1150°C.

- After sintering, at the former nanostructured grain boundaries a **different Cr concentration** is found, possibly due to **sensitization** and to the **localized overheating** induced by the **EM field concentration in the space between the particles.**

- Microwave sintering in multi-mode applicator provides **more homogenous parts, but with excessive grain growth**.

- Microwave sintering results are strongly affected by the nature and shape of the powders, as well as from the EM field distribution in the applicator, and this must be taken into account when scaling up or changing the sample geometry/composition

Acknowledgments to: Prof. Andrea Gatto, Dr. Elena Bassoli, Dr. Lucia Denti

And to you for your attention!

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http://www.mag.unimore.it