

## On-line tools for microscopic and macroscopic monitoring of microwave processing

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### Abstract

Direct monitoring of temperature, chemistry and microstructure is required to understand microwave heating in more detail, in order to fully exploit the unique features this non-equilibrium processing method can offer. In this paper, we show first that microwave radiometry can be used to follow volumetrically the thermal trajectory of microwave-heated aluminium powder. In-situ Raman spectroscopy is then shown to evidence thermal gradients between diamond and silicon grains in a binary powder mixture. Finally, perspectives and preliminary results of microstructural analysis obtained from X-ray microtomography are presented.

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### 1. Introduction

Microwaves are attractive for the processing of a broad variety of materials. Localised thermal gradients, unusual chemical pathways and “out-of equilibrium chemistry” are typically encountered. The ability to follow in-situ the evolution of an inorganic sample during its microwave processing still remains a challenge. Tools are needed to analyse and follow for example the volumetric temperature evolution. The detection of transient thermal gradients is of particular interest. They can occur at scales,

ranging from the sample's own dimensions (essentially due to resonant wave pattern) down to single grain size for heterogeneous or composite materials (due to the preferential electromagnetic energy dissipation in one of the sub-component). In addition, the detection of structural and chemical composition changes are also of great importance. Ideally, the sample thermal history should be collected as  $T(x, y, z, t, C)$ , where  $x, y, z$  represent the position of small volumes increments (voxels),  $t$  the time and  $C$  accounts for the chemical nature of the materials considered.

The electromagnetic field distribution in a material and the resulting heating pattern is influenced also by the morphology of the sample. It is therefore important to be

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able to follow as well the time-resolved evolution of the microstructure, namely the average porosity, as well as the grain size and constituent phase distributions.

## 2. Methods

The microwave radiometer used in this study is a hybrid low noise amplification described elsewhere [1]. Raman measurements were performed on a mixture of diamond and silicon powders. The spectrometer used is a Renishaw “in via”. More details are found elsewhere [2]. Preliminary microtomographic experiments on MW-treated silicon–diamond composites were performed at the MS-Beamline of the Swiss Light Source.

## 3. Results

### 3.1. Microwave radiometry

Aluminium powder (200 g) were placed in an insulating crucible and irradiated with 1 kW microwave radiation in a multimode cavity. The temperature was measured using an IR camera and a microwave radiometer, both systems fitted in the cavity. Due to the high sensitivity of the radiometer, the microwave irradiation was briefly interrupted to enable the radiometric evaluation. Fig. 1 shows the evolution of both temperature signals, as well as the amount of reflected microwaves. As opposed to the IR camera, the radiometer responds immediately, despite the thermal insulation. The thermal trajectory can be followed without delay. The radiometer used here is based on a single antenna and the radiometric temperature represents only an averaged signal. The presence of thermal gradients in the aluminium bed was proven experimentally determined as shown in Fig. 2. The maximal temperature is

reached at a depth of 40 mm. Considering the Kirchoff law, it is likely that the escape depth of microwaves spontaneously emitted from the hot powder bed is of the same order as the penetration depth of the incident microwave waves. The radiometer is thus able to detect temperature changes in the centre of the aluminium powder specimen.

### 3.2. Raman temperature measurements

A mixture of silicon and diamond powders was placed in an insulated quartz crucible. The composite powder is irradiated with microwaves. Fig. 3 indicates that a temperature gradient develops between the silicon grains and the diamond grains. The temperature of each phase is

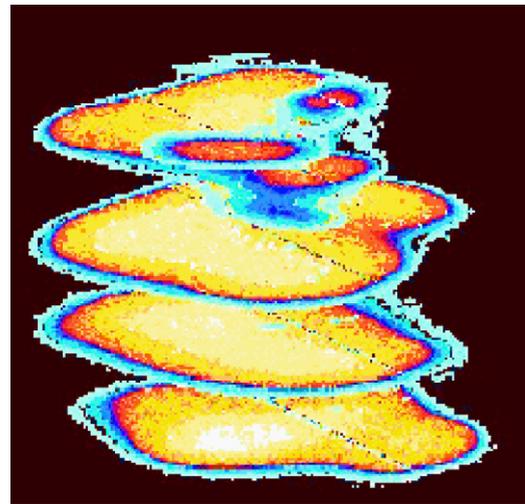


Fig. 2. Experimental relative temperature distribution in an aluminium powder bed ( $\varnothing$  80, depth 120 mm) at various depths: 20, 40, 60, 80, 100 mm.

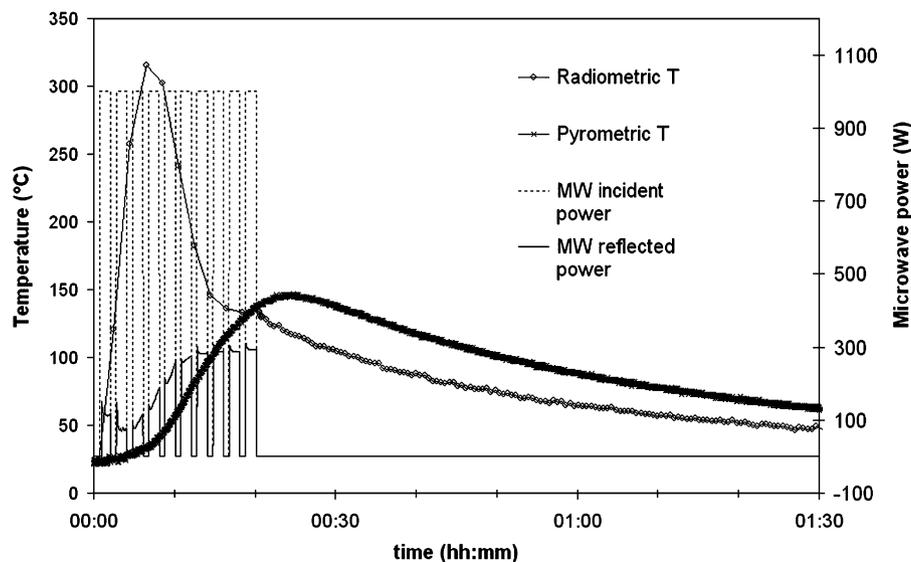


Fig. 1. Comparison of temperature measurement obtained from an IR camera and a MW radiometer for an aluminium powder sample placed inside an insulating layer.

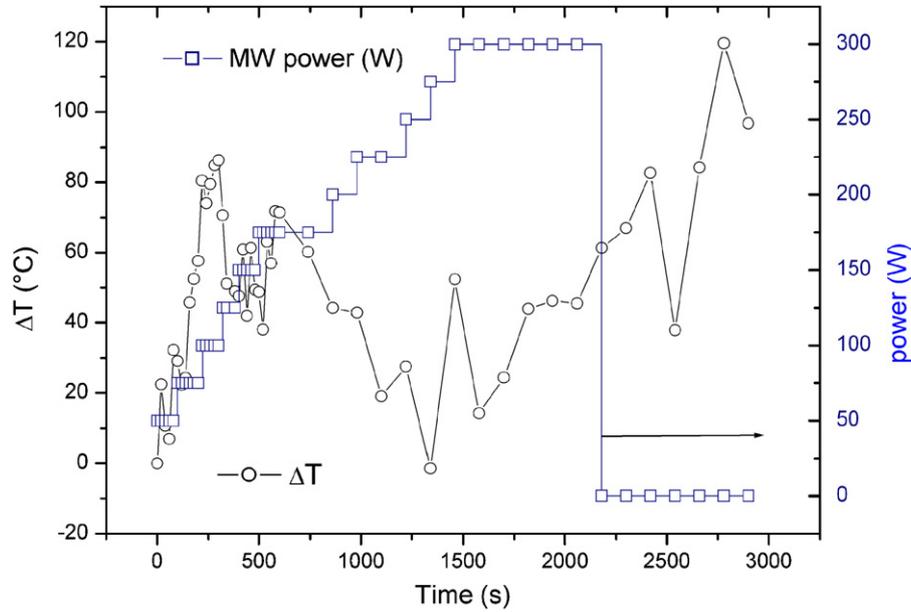


Fig. 3. Temperature difference obtained by Raman spectroscopy for a mixture of silicon and diamond powder under MW irradiation.

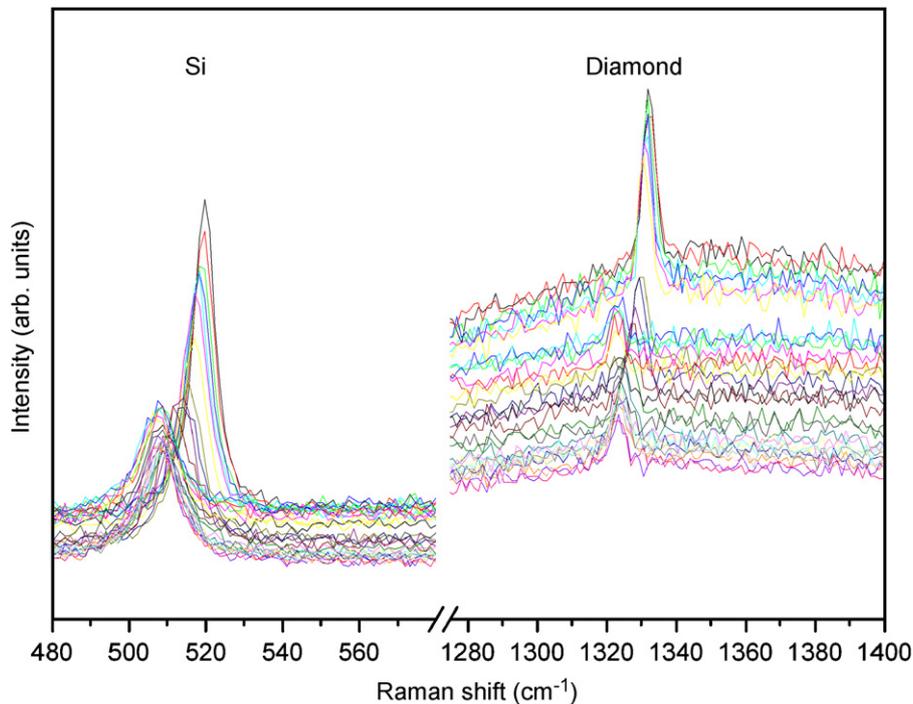


Fig. 4. Decrease of the Raman shift from 298 to 1273 K, for silicon and diamond.

obtained by measuring the shift of the Raman lines of silicon and diamond individually (Fig. 4). Raman spectroscopy enables the individual temperature measurement of silicon and diamond under microwave irradiation.

### 3.3. Preliminary microtomography experiments

Microtomography is a powerful method to visualise morphology changes inside a sample [3]. Fig. 5 shows an

electron micrograph of the surface of the silicon–diamond porous *composite* produced by microwave irradiation. The microstructure of the composite sample, obtained during a preliminary tomographic experiment, is represented in Fig. 6. These preliminary results confirm the feasibility of X-ray tomographic reconstruction and phase segmentation for this type of low *Z* materials. Further work is under-going in which tomography will be applied to follow the evolution of the microstructure.

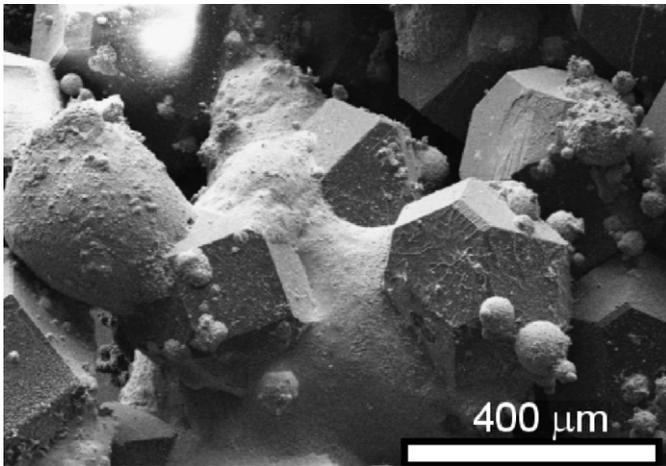


Fig. 5. SEM micrograph of a microwave processed silicon–diamond composite.

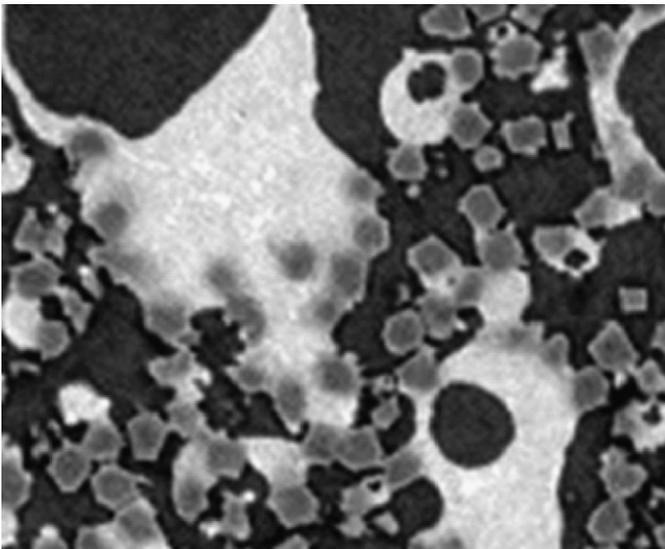


Fig. 6. Reconstructed cross-section of a silicon–diamond composite obtained from microtomography: black: porosity; dark-grey: diamonds; light-grey: silicon-rich phases.

## 4. Discussion

### 4.1. Temperature measurement tools upon microwave heating

One of the most crucial aspects of microwave heating is the accurate determination of the temperature distribution inside the material being processed since the lack of knowledge about the material's temperature changes is limiting the control of the microstructure and therefore of its properties. The electromagnetic wave inside the sample is a resultant of the incident wave (its amplitude and frequency) and the materials response. As the electromagnetic field within the material and the related absorbed

power shows noticeable time and space variations, so does the temperature distribution.

The commonly used thermocouple measurements do not provide reliable results since they provide the temperature of the metallic tip itself rather than that of the surrounding material. Moreover, the thermocouple placed within the specimen could interact upon heating with the applied electromagnetic field. Other temperature measurement tools being in contact with the specimen, like sensors based on luminescence effects can be used; however, the influence of the electromagnetic field on the quenching of the photon emission must be taken into account. Generally local-probe methods, if well adapted for samples at thermal equilibrium fail totally to account for any temperature heterogeneity.

Pyrometers and infrared cameras provide average values or the two-dimensional distributions of the local temperature field, respectively. However, both enable the temperature monitoring of the specimen's surface only. In low thermal conductivity materials, thermal gradients are more prone to arise. If a hot zone is developing, buried in the middle part of a sample, the risk is high that a detrimental event results by the time the surface of the sample reveals to the IR sensor that something has happened. This limitation becomes of particular significance given the common practice of placing a thermal insulation around the specimen to limit radiative heat losses. Another difficulty arises while considering the temperature dependence on the materials' emissivity. Each material is emitting infrared light in a different way; hence, the obtained temperature is not ultimate and actual measurements need to be completed by calibrations that may turn out impossible for reactive mixtures.

Spectroscopic techniques are able to discriminating temperature heterogeneities between different components of a mixture. In comparison to thermography, the collection of spectrally resolved infrared emission allows probing the absolute temperature collected from the inside of the specimen, independent from the sample's emissivity and gives, to some extent, information about changes in the specimen's composition, whenever the characteristic emission bands are known. This technique also offers a potential spatial resolution and sufficiently high signal to noise ratio for fast data acquisition.

In the case of the Raman spectroscopy the changing temperature fields may be observed by either recording the Raman peaks shifts or by monitoring the Stoke-to-anti-Stoke peaks areas, which change with temperature. The main advantage of this method is that the temperature can be found separately for each phase having its own, characteristic vibrational mode. In addition, Raman spectroscopy brings information both about the temperature and the evolution of chemical composition of the heated material.

Another promising technique, which can be implemented in-situ upon microwave heating, is powder X-ray diffraction. As diffraction patterns give information on the presence, volume fraction and lattice constant evolution

(thermal expansion) of a particular constituent phase upon heating, the temperature seen by each constituent phase can be retrieved. The use of this method is limited by the need for special-designed microwave furnaces and the requirement that the scattering signal is detected sufficiently fast to enable the accurate time-resolved acquisition of diffractograms with satisfactory counting statistics from specimens exposed to ultrafast microwave heating/cooling rates. However, the advent of high-brilliance synchrotron radiation sources and of fast X-ray detectors nowadays makes this a feasible task [4].

Nevertheless, none of the aforementioned techniques covers the desirable retrieval of a complete information data set  $[T(x, y, z, t, C)]$ ; however, different projections of the instantaneous temperature distributions are accessible via Raman, IR, radiometry or XRD.

#### 4.2. Tools for the evaluation of morphologic changes

As briefly presented, X-ray microtomography appears as one unique analytical method to visualise the kinetics of microstructure evolution, from which we hope to learn more about microwave specific materials synthesis pathways.

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