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Electromagnetic Field Processing of Materials at Microwave Frequency (2.45 GHz)

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Abstract
Microwave energy is applied to very wide areas in materials processing including calcinations, drying, synthesis, sintering, melting and brazing etc. The advantages of microwave processing such as time and energy savings, rapid volumetric heating leading to fine microstructures and improved mechanical properties, are well recognized. Microwave materials processing is also well recognized for exhibiting abnormal reaction kinetics in many systems and enhanced material diffusion during sintering. The cause of these effects has been attributed to, but not very well understood, the so-called ‘non-thermal or microwave effects’. Using a 2.45 GHz, single mode TE₁₀₀ cavity, it is possible to separate electric and magnetic components of microwave radiation and expose small size samples in almost pure E and H fields. This paper deals with materials processing under separate E and H fields at 2.45 GHz. The survey of variety of samples of metals, ceramics, composites and magnetic materials showed remarkable differences in their heating behaviors and microstructural developments. Certain materials when exposed to H-field were found to have de-crystallized in a few seconds. It is believed that not only magnetic field plays key role in this phenomenon of de-crystallization but also anisothermal situation causing localized large temperature gradients may also be responsible for such results.

Keywords: microwave magnetic field, phase transformations, de-crystallization

Introduction
The application of microwave energy to process various kinds of materials in an efficient, economic and effective manner is emerging as an innovative technology with great commercial potential and many attractive advantages. In the area of materials sintering and synthesis using microwave energy, substantial enhancements in the materials diffusion and reaction kinetics have been reported by many researchers all over the world. Almost all this work was conducted in multimode microwave systems in which the electric and magnetic fields cannot be separated. Recently, dramatic results obtained by the use of separation of electric and magnetic fields in a single mode cavity have confounded the scientific community working in this area, and it presented new insights to help in understanding the mechanisms of microwave-matter interactions.

Cherradi et al. [1] claimed for the first time that in many ceramics the dielectric loss mechanism was a minor contribution to the power absorbed compared to the induction losses caused by eddy currents. These researchers also attributed the heating of metals only to eddy current losses from the H field of the microwave e/m radiation. In the Penn State’s recent work [2], a survey of a variety of samples of metals, ceramics and composites, showed remarkable differences in their heating behavior depending upon whether they were exposed to E field or H field at 2.45 GHz. All metals were very effectively and rapidly heated in the H field but not in the E-field, the reverse was true in case of insulators or ceramics. Further only powder metals could be heated; a solid metallic rod did not get heated at all in either field. Endo et al [3] have shown that two crystalline solid phases could be reacted
to give a non-crystalline solid without melting. They achieved this result by exposure of the mixed phases to a 28GHz microwave field in a multimode cavity for 1-2 minutes typically. The phases they studied were all ceramic phases – typically ferrites such as CoFe₂O₄, ZnFe₂O₄, BaFe₁₂O₁₉, etc. This work now has been expanded to study the effect of field separation on the solid phase-transformations in the materials of various conductivities. This paper briefly describes these results.

Experimental

In a multi-mode microwave systems operating at 2.45 GHz frequency various modes of the electric and magnetic components of electromagnetic field are mixed and homogenized. Therefore, in a multi-mode cavity configuration the E and H fields can not be separated. However, in a single mode cavity the E and H distributions can be fixed. For example, in a TE₉₀₃ single mode cavity electric and magnetic fields can be separated and materials can be exposed to reasonably pure E and H fields at 2.45 GHz. In an unloaded cavity where E is maximum, H is zero, and where H is maximum, E is zero (Figure 1). Therefore small samples placed at E or H nodes will experience either H field or E field, respectively. Pellets of the sample (dia. 0.25-0.5 cm and 1-2 mm thick) are introduced into single mode cavity, and the appropriate power adjusted as needed from ~100W to 2000W depending on the material and the size. After exposure to the 2.45 GHz beam for ≈1 second to ≈3 minutes the sample is removed and examined by XRD, SEM, TEM, Raman, etc.

![Electric field distribution](image1)

![Magnetic field distribution](image2)

Figure 1. The microwave field distribution inside the TE₉₀₃ single-mode cavity.

![Pure Fe₂O₃ in E field](image3)

![Pure Fe₂O₃ in H field](image4)

Figure 2. The XRD patterns of Fe₂O₃ exposed in E and H fields.

Results

The detailed results have been reported elsewhere [4-7]. Hereunder, we only give brief summary of this work.

Figure 2 and 3 show XRD patterns and SEM photos of Fe₂O₃ exposed in E and H fields respectively. It is obvious that crystalline magnetite phase transforms totally into de-crystalline form in H-field but remains crystalline and gets oxidized to become Fe₂O₃ in E field.
Small pellets made of the stoichiometric mixture of BaCO$_3$+4Fe$_3$O$_4$ were irradiated in the E and H fields. Figure 4 and 5 show the respective SEM photos and XRD patterns indicating that formation and de-crystallization of Ba-ferrite has occurred in H-field, however, exposure to E-field produces crystalline Ba-ferrite. Similar results were obtained in other ferrites also: such as NiFe$_2$O$_4$, ZnFe$_2$O$_4$, and CoFe$_2$O$_4$. 

Figure 3. The SEM images of Fe$_3$O$_4$ exposed in E and H fields.

Figure 4. The XRD patterns of BaCO$_3$+Fe$_3$O$_4$ exposed in E and H fields.
The data on the magnetic properties of these materials show that while the ferrites made in the multimode chambers and E-field (in single mode) have the usual wide hysteresis loops, all the materials treated in the H-field immediately collapse to become soft-magnets. ZnFe$_2$O$_4$ transforms from antiferromagnetic to ferromagnetic.

CuO and MnO$_2$ exhibit the same phenomenon that is when exposed to H-field they transform partially into amorphous state. This shows that the de-crystallization phenomenon is not associated only with ferromagnetism (magnetic materials). The SEM photos of the de-crystallized CuO and MnO$_2$ in H field are shown in Fig. 6. The most peculiar CuO microstructures have not been analyzed and repeated several times as yet but the unusual periodic stripes are seen again in the MnO$_2$ microstructure. A sample of pure crystalline Pr$_6$O$_{11}$ (a common rare earth with the fluorite structure) showed stepwise de-crystallization again in H field only (Figure 7). In all these oxides E field does not produce any de-crystallization effect.

Figure 6. The XRD patterns and SEM images of CuO (a) and MnO$_2$ (b) exposed in H field.
A pellet is made of pure TiO\textsubscript{2} which was slightly reduced in 90% N\textsubscript{2}, 10% H\textsubscript{2} atmosphere at approx. 1000°C to give TiO\textsubscript{2-x}. The pellet is placed in the H field at a power of 900W and the reaction was stopped at successive short intervals. The data of Fig. 8 show again the step-wise nanosizing and ultimate de-crystallization of TiO\textsubscript{2}. BaCO\textsubscript{3} is mixed with TiO\textsubscript{2-x} and pelletized and reacted. The same microwave exposure leads to a de-crystallized product.

**Discussion**

Endo et al. [3] explained this observation in magnetic materials in terms of their magnetostriction constant, that higher was the magnetostriction constant lower microwave power was required to de-crystallize the material. But this can not explain the de-crystallization of non-magnetic materials. The ceramic oxides which de-crystallized in microwave magnetic field had one thing common: all had unfilled 3d or 4f electronic shells with unpaired electrons. This may explain partially the interaction of magnetic field with the unpaired electron spins to transform the material into electronically an excited
state, and then the coupling/interaction with the lattice to disrupt the crystallinity. An exact detailed mechanism of this interaction has not yet been developed. Another explanation in case of multi-phase systems is the selective heating of one phase over the other due to different microwave absorption rates resulting in to a large temperature difference between the phases. This localized an-isothermal situation in a microwave field can cause drastic enhancements in the reaction and diffusion kinetics [8]. This has been demonstrated by using a digital microscope. A visual movie image in-situ was observed of the heating process of powder consisting Fe₃O₄ and BaCO₃ by microwave H-field [9]. Random generation, movement, and disappearance of hot spots in the order of 100 micron were observed throughout duration of a few seconds. The temperature, size, shape, and the duration of the hot spots maintained certain regularity. This is the first case in the world of capturing formation of micron scale strong thermally non-equilibrium or localized temperature gradients (a few hundred °C/100 micron, a few thousand °C/mm) system during heating.

How does the magnetic (or electric) field couple to the crystalline phase and how does it create the electronically excited state as noted above, is an important issue which needs further investigation.

According to a standard textbook on interaction of microwaves with matter the microwave power absorbed per unit volume (P in W/m³) is expressed by the equation:

\[ P = 2\pi f_0 \left( \varepsilon_0 \varepsilon'' E^2 + \mu_0 \mu'' H^2 \right) \]

where E and H are the electric and magnetic fields, \( f_0 \) is the frequency, \( \varepsilon'' \) & \( \mu'' \) dielectric and magnetic loss factors respectively. However, in the vast literature on theories of microwave-matter interaction, the magnetic field effects have been totally ignored. Magnetic fields do interact with matter and have profound effects as shown above. These experiments clearly show that the microwave electric and magnetic field supplied the energy directly to the material to make chemical process, such as reduction and heating. It is clear that high frequency magnetic fields will be a potential new vector in semiconductor and optical device manipulations.

References