37th Cement and Concrete Science Conference
11-12 September 2017
University College London

Thermal and Non-thermal Effects of Microwave on Metal and Metal Oxide – A Critical Review

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ABSTRACT

As a promising alternative to the conventional thermal heating methods, microwave heating has advantages such as volumetric heating and fast heating rate. However, the effect of microwave on the material is still controversial. This paper gives a critical review on the thermal and non-thermal effects that microwave may have on metal and metal oxides. Under thermal effect, the factors contributing to hot spot, magnetic heating and microwave discharging are thoroughly reviewed, whilst under the non-thermal effect, the change of chemical reaction process, nanostructure and electronic structure of metal and metal oxide under microwave irradiation are carefully discussed.

1. INTRODUCTION

Microwave heating has several advantages over conventional heating methods including volumetric heating, fast heating rate, automatic control and environmentally friendly nature. With these advantages, therefore, microwave heating has been applied into many fields such as sintering of ceramics and metals, curing of polymers, chemical synthesis, mineral processing and accelerated concrete curing [1].

Table 1. Application of microwave heating in the metal and metal oxide [2]

Field	Application
Chemical processing	Microwave-assisted solid-state reactions using metal powders
	Microwave-assisted liquid-phase reactions using metal powders
mineral	Heating of iron-ore-carbon
	Direct steel-making from iron-ore using microwave-assisted hybrid heating
sintering	pyrolysis of metallorganics
	sintering of ceramics, metal sintering
Photo-chemistry	TiO_2 catalysts

It is a well-known fact that metals, being good conductors, cannot be heated significantly using microwaves. However, microwave heating can be applied in metallic materials under specific conditions. Considerable reviews on the application of microwave heating in metal and metal oxide have been published. Table.1 summarises the application of microwave heating in the metal and metal oxide. However, a detailed review to clearly distinguish the thermal and non-thermal effects that the microwave irradiation may have on the metal and metal oxide is still missing, even though a good understanding on the interactions between microwave and metal or metal oxide is considered essential for the development of a microwave-based curing technique for manufacturing reinforced concrete products, an area which has been attracting lots of attentions worldwide.

This paper, thus, presents a detailed review on some specific effects that the microwave may have on metal or metal oxide including specific **thermal effect** (hot spot, magnetic heating and microwave discharging) and **non-thermal effect** (chemical reaction process, nano-structure and electronic structure of metal and metal oxide). It is anticipated that this information might benefit the development of a microwave-based curing technique for reinforced concrete.

2. The mechanism of microwave heating on metal and metal oxide

The fundamental mechanism of microwave heating is the interaction between microwave and materials under microwave irradiation, which is distinct from conventional thermal heating methods, and is generally divided into three types: (i) dielectric heating, (ii) conduction loss heating, and (iii) magnetic loss heating. The dielectric heating and conduction loss heating result from the electric part of microwave while the magnetic loss heating is caused by the magnetic part of microwave. Dielectric loss heating is the main mechanism for solution while most solid metal and metal oxide materials is dominated by conduction loss heating. Magnetic loss heating is only to be expected in magnetic (solid) materials such as Fe_3O_4.

At the molecular level, the dielectric heating by microwave is due to the molecular friction and collisions by dipolar and interfacial polarization [3]. The conduction loss is often enhanced by increased collision rate of the electrons and ions under the influence of an electric field, resulting in the consumption of energy [4]. In magnetic materials, magnetic losses such as hysteresis, eddy currents, domain wall and electron spin resonance contribute to the heating [2]. The thermal energy P produced per unit volume from microwave irradiation is provides by Eq.1 [2].

$$P = \pi f \varepsilon_0 \varepsilon'' |E|^2 + 1/2\, \sigma |E|^2 + \pi f \mu_0 \mu'' |H|^2 \quad (1)$$

where $|E|$ and $|H|$ denote the strength of the electric field and magnetic field of the microwaves, respectively; σ is the electrical conductivity; f is the frequency of the microwaves; ε_0 is the permittivity in vacuum; ε'' is the dielectric loss factor; μ_0 is the magnetic permeability in vacuum; and μ'' is the magnetic loss.

3. Thermal effect on metal and metal oxide

Based on the above fundamental heating mechanisms, several specific thermal effects in metal and metal oxide exist including hot spot, magnetic heating and microwave discharging.

3.1 Hot spot

Although volumetric uniform heating is the most prominent advantage of microwave heating over other heating methods, sometimes microwave heating cannot be considered as homogenous heating in a system mixed with different dielectric materials. The reason is that the inhomogeneous electromagnetic distribution field in different dielectric materials leads to the inhomogeneous distribution of temperature, resulting in 'hot spot'. The definition of 'hot spot' is the local overheating area. Zhang *et al.* [5] proposed three conditions which are needed for the formation of 'hot spot', namely: (1) dielectric materials with different loss tangent distributed inhomogeneously; (2) The distribution of microwave is inhomogeneous; (3) The heat transfer rate of reactants are different.

3.2 Magnetic heating

Since magnetic materials are almost metal (magnetic metal) or metal oxide (semiconductive metal oxide), magnetic heating often occurs in metal and metal oxide. The high magnetic loss factor of these magnetic materials results in the high absorption of magnetic part of microwave, while for the other dielectric materials the absorption of electric part of microwave is the main source for heating [6].

3.3 Microwave discharging

Besides the heating effect mentioned above, microwave irradiation also alters the distribution of the positive and negative charges on the conducting materials. Subsequently, electrical discharge by microwave often occurs on metals with sharp edges. Depending on the factors such as gas pressure, discharges can be classified into several types such as corona discharge and electric spark with current–voltage characteristics (Figure.1) [7].

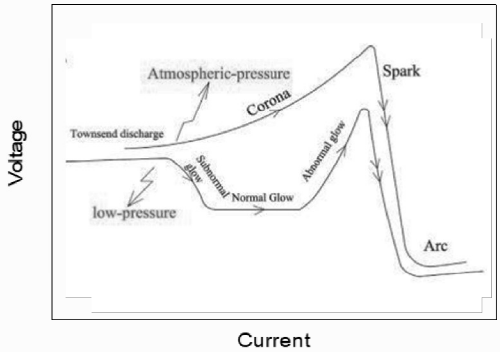

Figure 1. Schematic current–voltage characteristics of the different types of discharges in gases.

Due to the transient and concentrated discharging process, temperature goes up locally and thus 'hot spot' appears. Moreover, the chemical reaction process and subsequent product composition is also possibly affected by discharging.

4. Non-thermal effect on the chemical reaction process

Generally, there are two main viewpoints on the microwave heating effect: some argue that the acceleration is only the result of specific thermal effect of microwave heating while the others support the non-thermal effect of microwave [8].

4.1 Activation energy and Pre-exponential factor

Among the evidences of non-thermal effect, the considerable increase of chemical reaction rate is mostly reported as a proof [2,9,10]. According to Arrhenius' equation (Eq.2), microwave could change the value of pre-exponential factor *A* [10] and activation energy E_a [2,9], which leads to the increase of chemical reaction rate *K*. In the equation, *T* is the absolute temperature and *R* is the universal gas constant.

$$K = Ae^{-E_a/RT} \tag{2}$$

The reduction of activation energy is observed in several metallurgical systems such as sintering of alumina ceramics [2]. The possible mechanism is the alignment of molecules (entropy effect) [9] due to microwave irradiation leads to the reduction of activation energy, that is, the minimum energy required to start a chemical reaction is reduced.

However, in some reports the activation energy under microwave is the same as that under conventional thermal heating [ref?]. Nevertheless, the pre-exponential factor of reaction always proves to be different between microwave heating and conventional heating [10].

$$A = \gamma\lambda^2\Gamma \tag{3}$$

Where *A* is pre-exponential factor, γ is a geometric factor which includes the number of nearest-neighbour jump sites, λ is the distance between adjacent lattice planes, i.e. the jump distance, and Γ is the jump frequency [10].

$$\Gamma = \nu \exp(-\Delta G^{+}/kT) \tag{4}$$

The influencing factors of the jump frequency Γ is shown in Eq.4. where v is the natural vibration frequency of the atoms, and ΔG^{+} is the activation energy. Since ΔG^{+} seems difficult to change, it is possibly for microwave to affect v , especially for phenomena relying on diffusion along grain boundaries or across surfaces where frequency factors are less well defined [10].

It should be noticed that the energy of microwave photon is about 10^{-5} eV at a frequency of 2.45 GHz which is lower than the energy of chemical bonds like covalent or even Van der Waal bonds [11]. Therefore, absorption of the microwave photon should not cause breakage of chemical bonds but influence the process of new chemical bond formation.

4.2 Transport in chemical reaction process

In addition, species transport also influences the chemical reaction process. The rapid nucleation and dissolution is observed in the titanium [10] and aluminium compound [12].

Rybakov and Semenov [13] reported that a microwave electric field induces a nonlinear driving force for mass transport near free surfaces, interfaces and grain boundaries in ceramic materials. This additional driving force leads to enhanced mass transport.

5.Non-thermal effect on the nanostructure and electronic structure

The different reaction kinetics not only contributes to the acceleration of chemical reaction rate, but the nanostructure and electronic structure of some system is also changed under microwave irradiation.

For some ferromagnetic oxides such as CuO containing 3d ions, a solid-state phase transformation from a crystalline phase to a non-crystalline phase (decrystallization) is observed. Ferromagnetism is required for decrystallization possibly due to the presence of d and f electrons in the electronic structure of ferromagnetism materials which provide two valence states giving rise to charge transfer or narrow d-bands under magnetic field part of microwave [14].

The electronic structure of semiconductor determines the conductivity of semiconductor and thus sometimes influences the reaction process related to the semiconductor. Electronic structure change due to microwave is reported in some literatures. Warman *et al.* [15] showed that the oxygen vacancies was formed at the interfacial boundaries between the coupled rutile and anatase polymorphic structures of P25 TiO_2 semiconductor.

6. Relationship between thermal and non-thermal effect

Some authors refuted the presence of non-thermal effects, claiming the far more acceleration of microwave heating than conventional heating methods under so-called identical temperature history is just a result of inaccurate temperature measurements [16]. However, even if reliable and accurate knowledge of the sample temperature is ensured, significant difference between microwave and conventional heating still exist [17].

Apart from the temperature measurement reasons, a wide range of materials with diverse chemical and physical properties in the reports of microwave heating may lead to either thermal effect or non-thermal effect of microwave, that is, the excitation of the rotational motion of molecules could transform into heat or efficiently transform to the chemical energy without dissipating to heat.

7. CONCLUSIONS

This review provides a critical analysis of the thermal and non-thermal effects of microwave on the metal and metal oxide. In terms of thermal effect, due to the selective heating of different materials, hot spot appears sometimes. On the other hand, since some metal and metal oxide are magnetic materials, magnetic heating could also exist; Additionally, being a good conductor, electric discharging is possible at the sharp edge of metal which could cause localized high temperature. In regards to non-thermal effect, the activation energy and pre-exponential factor could be changed due to molecular influence of microwave; The nucleation and dissolution process of reaction are enhanced by microwave; Magnetic part of microwave may also lead to the decrystallization of oxides; Finally, the reason for the controversy of the thermal and non-thermal effect is discussed.

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