Rapid communication

Neck formation between copper spherical particles under single-mode and multimode microwave sintering

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This paper presents results of an investigation concerning neck formation during microwave sintering of copper powder. Porous copper samples were treated in single-mode and multimode microwave furnaces in order to investigate neck formation process. Samples were heated to temperatures as high as 0.8\textsuperscript{T}_{mp} in 2.45 GHz microwave field. Evidence of pure microwave effect on initial stage of sintering was found on fracture surface of sintered samples, as development of micro-plasma discharges in porous material seem to enhance sintering process.

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1. Introduction

Microwaves have found a broad application in different branches of industry replacing some conventional heating technologies. Microwave processing provides possibility to achieve uniform and fast heating in compacts through microwave heating [1]. Microwaves directly interact with the particles within the pressed compacts and thereby provide rapid volumetric heating [2]. This reduces processing times and results in energy saving. In addition, the uniform heating minimizes problems such as localized microstructural coarsening and non-uniform sintering, thereby yielding better overall properties. Traditionally microwaves have been used to sinter ceramics, refractory materials as well as ferrites [2], but for past decade microwave processing has been found applications in new fields such as metals. It is well known, that bulk metals are reflectors of microwaves, though, it was shown that metals could couple with microwaves too, provided the metals are in powder form rather than monoliths [3].

However, as compared to ceramics, microwave sintering of particulate metals and alloys has increased in popularity only recently [4]. Though there have been attempts to explain microwave heating of metal powders, there is still not a consensus on a comprehensive theory to explain the mechanism of heating of metals in microwave field.

The microwave heating of materials is based on energy dissipation due to an internal friction of atoms/molecules, charges or defects present in the material being exposed to microwave radiation [5]. This friction is produced if the ion cannot quite keep moving with a high frequency electromagnetic field (insulators with dielectric losses), while no friction is produced if ion cannot move at all (perfect insulators), or if it moves too easily (conductors). Very little heating occurs when microwaves are reflected by material samples (such as bulk metals), or penetrate through the material samples with no or little dielectric loss.

Since usage of microwave energy for heating of conductive materials in porous state is possible, it has become possible to conduct model experiments on initial stage of sintering using microwaves. The aim of this work is to clarify the effect of MW heating on initial stages of sintering of metal powder compacts, based on the results of fracture surface of samples sintered in pure microwave sintering in multimode and single-mode furnaces.

2. Experimental procedure

For model experiments in microwave commercially available Copper powder was used (Alfa Aesar-Lot #42623). Prior to pressing,
powder was checked for particle's size distribution (MasterSizer 2000, Malvern).

Green pallets with a dimension of 6 mm in diameter and 3 mm in height were pressed in a steel die with 100 MPa of uniaxial pressure. The microwave sintering experiments were conducted by using a 6 kW, 2.45 GHz multimode microwave cavity and 2 kW 2.45 GHz single-mode cavity. No susceptors were used in the experimental setup, as to refer heating to pure microwave heating. A schematic drawing of experimental setup for multimode applicator is presented in Fig. 1.

To avoid additional errors in electromagnetic field distribution and temperature measurements [6] the temperature was monitored using infrared pyrometer Raytek MA2SC (working temperature range 350–2000 °C) and recorded in situ by a computer. After the sintering temperature was reached, the isothermal holding was applied. After cooling, density of the specimens was calculated by dimension and weight measurements, and by the Archimedes method. Samples with similar final density were chosen and then fractured after holding in liquid nitrogen to provide brittle fracture and were examined by SEM (Hitachi S-3500N) for their microstructures.

3. Results and discussion

The general temperature–time profiles of sintering experiments of copper samples in multimode and single-mode microwave sintering are presented in Fig. 2. As pyrometer starts recording of temperature from 350 °C, it may take up to 10 min to heat up copper sample in multimode furnace, though for single-mode quick almost immediate heating was recorded during processing. This was due to the fact that in a single-mode cavity the energy is quite intense and concentrated around the specimen. Heating to set temperature was made possible by controlling the power for both cases (200W for single-mode, and 1.0 kW for multimode), the microwave generator power level was suitably reduced to get constant temperature for soaking period.

For sintering experiments narrow particle size distribution is desirable as it allows observation of size changes during sintering process. Copper powder used in this experiments was characterized by distribution (Fig. 3) with standard deviation of 0.51 and mean and average size of 126 and 120 μm. EDX of sintered sam-

Fig. 1. Experimental setup for multimode microwave furnace.

Fig. 2. The temperature–time profiles of the experiments during microwave sintering of copper compacts in multimode and single-mode microwave furnace.

Fig. 3. Particle size distribution of copper powder.
samples showed little, if any, oxidation of surface of samples, which may show that usage of N\textsubscript{2} + 5\% H\textsubscript{2} gas mixture results in additional surface reduction from oxides.

To clarify nature of initial stage sintering, formation and analysis of contact zones, fracture surfaces of samples sintered in multimode and single-mode microwave furnace were presented in Figs. 4 and 5.

After initial contacts are made by pressing of precursor powder, during short soaking contacts get larger in size and their number may change during sintering process. In contrast to conventional sintering, where contacts get formed of solid flat cylinders, during microwave processing the cylinders are rather porous with foam-like structure in contact zone (Fig. 4c and e). Such difference may occur due to abnormal growth of diffusion activity of atoms. Mass transport enchantment was previously reported for microwave sintering process [7,8]. It is due to fact that mass transport process is affected by non-thermal interaction of electromagnetic field with material and therefore diffusion coefficient were reported to be higher while microwave heating is applied [8].

There could be few explanations for this phenomenon. First if one assumes that the temperature in contact zone doesn’t increase rapidly, such growth in diffusion activity has non-thermal nature and can be a consequence of reaction diffusion, which, in fact, could lead to so-called “microwave effects” [9], as were reported for vast majority of ceramic materials rather then for metal ones.

Partial melting was observed in contact zone, due to the fact that the strength of MW field is higher than in the rest of the particle [10]. This may favor evaporation of some volume of necks and thereby partial neck growth by evaporation-condensation mechanism. Where evaporated atoms condense in the neck region in order to satisfy Kelvin equation.

Generation of eddy currents during microwave processing of metals was also previously investigated. Those are caused when a conductor is exposed to a changing magnetic field due to relative motion of the field source and conductor; or due to variations of the field with time. The stronger the applied magnetic field, or the greater the electrical conductivity of the conductor, or the faster the field that the conductor is exposed to changes (frequency factor in case of microwave heating), then the greater the currents that are developed and the greater the opposing field. In a recent work [11] it was shown that, green copper samples are heated readily by induced eddy currents generated by 2.45 GHz H-field. And as particles heat up, contacts are formed and fractional volume of the compact subjecting to eddy currents is reduced.

Another study [12] suggests that heating of the area close to the surface of the individual powder particles due to the skin effect and the electric high frequency fields between the individual powder particles may generate micro-plasmas during microwave heating of metals either at the grain boundaries or inside the pores. Local plasma may sputter material away to the pore area of the powder arrangement. Thus the transport into the contact area takes place via finest particles in the gas phase. As the size of particles in contact is sufficiently decreased, it may lead to higher sintering activity, high enough to start sintering of material at relatively lower temperatures. Further, those tiny particles on initial particles surface may support neck formation and growth which lead to shortening of initial stage sintering.

There is an increase in connection intensity of the particles (Fig. 4e), as well as densification degree in compact in contrast to zones that where formed during uniaxial pressure (Fig. 4c and d). Therefore structure of contact zones for microwave sintered samples may be similar to neck structure that is formed via “self-adjusting” mechanism for Spark Plasma Sintering (SPS) [13]. Where neck growth is accelerated on initial stage and then suppressed due to geometrical factor that does not favour current flow thought powder system, and supporting particle rearrangement during sintering process. It is quite likely that all these mechanism may be taking place simultaneously.

Thus, it was important to compare neck formation process with usage of single-mode furnace operating at the same frequency and temperature conditions. One can clearly see (Fig. 5a, c and d), that during heat treatment in a single-mode applicator, the particles themselves change form, and become more elongated. This could be a consequence of additional particle movement, or specific driving force of sintering process during microwave heat-treatment. Microwave sintering in single-mode cavity allows us to have stronger EM field distribution in cavity and better coupling (heating) (Fig. 2), and also has better efficiency of energy transfer. As for as use of no susceptor is concerned during sintering process, nature of necking process for sintering in single-mode may.
be the same as discussed above. But better heating efficiency and shorter processing times may suggest that plasma ignition between particles may take place as the result of quick creation of eddy currents on the surface and possible surface-charge discharging to free space between packed particles to enhance necking and heating processes.

Other possibility to identify diffusion mechanism during sintering process is research of neck growth during initial stage sintering of microwave process, or measurement of specific surface area reduction during sintering process, which may be considered as next step in future research.

4. Conclusions

Model experiments on microwave sintering of copper samples were conducted. Pure microwave heating in both single-mode and multimode applicators was applied at 2.45 GHz. Fracture surface of samples showed traces of plasma discharging, thus showing clear effect of microwaves on sintering process. However research in classical neck growth kinetics is vitally needed for predominant diffusion mechanism identification.

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References