MICROWAVE-ASSISTED SYNTHESIS OF NANOMATERIALS AND NANOCOMPOSITES

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Abstract: The use of emerging microwave (MW)-assisted chemistry techniques in conjunction with greener reaction media is dramatically reducing chemical waste and reaction times in the production of nanomaterials and nanocomposites. This paper summarizes our own experience in developing MW-assisted chemical synthesis methods for nanomaterials and nanocomposites.

KEYWORDS: Noble Nanometals, Carbon Nanotubes, Cross-linking, Renewable polymer, Nanocomposites.

MW-Assisted Shape-Controlled Bulk Synthesis of Ag and Fe Nanorods in Polyethylene Glycol (PEG) Solutions

Recently we have accomplished bulk syntheses of Ag and Fe nanorods using PEG under MW irradiation conditions [1]. Favorable conditions to make Ag nanorods were established and the process was extended to make Fe nanorods with uniform size and shape. The nanorod formation depended upon the concentration of PEG used in the reaction with Ag salt. Ag and Fe nanorods crystallized in face centered cubic symmetry. The method uses no surfactant or reducing agent and is greener in nature which could open a myriad of applications. In a typical procedure, aqueous silver nitrate (AgNO₃) solution (0.1 M) and different mol ratios of PEG (molecular weight 300) were mixed in a 10 mL test tube at room temperature to form a clear solution. The reaction mixture was irradiated in a CEM Discover focused MW synthesis system maintaining a temperature of 100 °C (monitored by a built-in infrared sensor) for 1 h with a maximum pressure of 280 psi. The resulting precipitated Ag nanorods were then washed several times with water to remove excess PEG. Control experiments were conducted in an oil bath at 100 °C for 1 h, at the temperature reached in the MW system. The obtained Ag nanorods are shown in Figure 1.



Figure 1. SEM images of Ag nanorods obtained via MW irradiation for 1 h using (a) 4 mL PEG + 4 mL AgNO₃, (b) 5 mL PEG + 3 mL AgNO₃, and (c) 3 mL PEG + 5 mL AgNO₃.

MW-Assisted Synthesis of Noble Metals Using Natural Polymers

Bulk and shape-controlled synthesis of gold (Au) nanostructures with various shapes such as prisms, cubes, and hexagons was accomplished via MW-assisted spontaneous reduction of noble metal salts using an aqueous solution of α -D-glucose, sucrose, and maltose [2]. The expeditious reaction was completed under MW irradiation in 30-60 s and can be applied to the generation of nanospheres of Ag, Pd, and Pt (see Figure 2 for TEM images). The noble nanocrystals underwent catalytic oxidation with monomers such as pyrrole to generate noble nanocomposites, which have potential functions in catalysis, biosensors, energy storage systems, nano-devices, and other ever-expanding technological applications. In a typical experiment, an aqueous solution of HAuCl₄ (0.01 N) was placed in a 20 mL glass vessel and mixed with an appropriate amount of α -D-glucose. The reaction mixture was exposed to high-intensity MW irradiation (1000 W, Panasonic MW oven equipped with invertor technology) for 30-45 s. Similarly, experiments were conducted using 0.01 N PtCl₄, 0.01 N PdCl₂, and 0.1 N AgNO₃.



Figure 2. TEM images of Au nanostructures synthesized (low concentration of sugar) using MW irradiation with natural polymers such as (a) sucrose, (b) α -D-glucose, or (c, d) maltose. The insets show corresponding electron diffraction patterns.

MW-Assisted Synthesis of Carboxymethyl Cellulose (CMC) /Metal Biodegradable Nanocomposites

A green approach was established that generated bulk quantities of nanocomposites containing transition metals such as Cu, Ag, In, and Fe at room temperature using a biodegradable polymer, carboxymethyl cellulose (CMC), by reacting respective metal salts with the sodium salt of CMC in aqueous media [3]. These nanocomposites exhibited broader decomposition temperatures when compared with control CMC, and Ag-based CMC nanocomposites exhibited a luminescent

property at longer wavelengths. The noble metals such as Au, Pt, and Pd did not react at room temperature with aqueous solutions of CMC, but did so rapidly under MW conditions at 100 °C. This environmentally benign approach, which provides facile entry to the production of multiple shaped noble nanostructures without using any toxic reducing agent such as sodium borohydride (NaBH₄), hydroxylamine hydrochloride, and so forth, and/or a capping/surfactant agent, and which uses a benign biodegradable polymer CMC, could find widespread technological and medicinal applications. The ensuing nanocomposites derived at room temperature and MW conditions were characterized using scanning electron microscopy, transmission electron microscopy, infrared spectroscopy, UV-visible spectroscopy, X-ray mapping, energy-dispersive analysis, and thermogravimetric analysis.

Preparation of Novel Metallic and Bimetallic Cross-Linked Poly (vinyl alcohol) (PVA) Nanocomposites under MW Irradiation

A facile method utilizing MW irradiation was achieved that accomplished the cross-linking reaction of (PVA) with metallic and bimetallic systems [4]. Nanocomposites of PVA cross-linked metallic systems such as Pt, Cu, and In, and bimetallic systems such as Pt-In, Ag-Pt, Pt-Fe, Cu-Pd, Pt-Pd and Pd-Fe were prepared expeditiously by reacting the respective metal salts with 3 wt. % PVA under MW irradiation, maintaining the temperature at 100 ^oC, a radical improvement over the methods for preparing cross-linked PVA described in the literature. The general preparative procedure is versatile and provides a simple route to manufacturing useful metallic and bimetallic nanocomposites with various shapes, such as nanospheres, nanodendrites and nanocubes.

MW-Assisted Synthesis of Noble Metal Decoration and Alignment of Carbon Nanotubes (CNT's) in CMC

A facile MW method that accomplishes alignment and decoration of noble metals on carbon nanotubes (CNT) wrapped with CMC was demonstrated. Carbon nanotubes such as single-walled nanotubes (SWNT), multi-walled nanotubes (MWNT), and Buckminsterfullerene (C-60) were well dispersed using the sodium salt of CMC under sonication[5]. Addition of respective noble metal salts then generated noble metal-decorated CNT composites at room temperature. However, aligned nanocomposites of CNTs could only be generated by exposing the above nanocomposites to MW irradiation. The general preparative procedure is versatile and provides a simple route to manufacturing useful metal coated CNT nanocomposites (see Figure 3).



Figure 3. Aligned CNTs in CMC polymer matrix.

MW-Assisted Synthesis of Cross-Linked PVA Nanocomposites Comprising SWNTs, MWNTS, and C-60

The cross-linking reaction of PVA with SWNTs, MWNTs, and C-60 using MW irradiation afforded nanocomposites of PVA cross-linked with SWNT, MWNT and C-60 expeditiously by reacting the respective carbon nanotubes with 3 wt.% PVA under MW irradiation and maintaining a temperature of 100 ⁰C; this represents a radical improvement over literature methods to prepare such cross-linked PVA composites [6]. The general preparative procedure is versatile and provides a simple route to manufacture useful SWNT, MWNT and C-60 nanocomposites.

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Microwave-assisted Synthesis of Monodispersed Nickel Nanoparticles Using Complex of Nickel Formate with Long-Chain Amine Ligands

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Abstract

We have successfully prepared face-centered cubic (fcc) Ni nanoparticles by the reduction of Ni²⁺ ion contained in its formate complex having the long-chain amine ligands through the thermal decomposition within a short time under microwave irradiation. The reduction in the presence of the long-chain amine ligands was promoted at lower temperatures than that in the absence of the ligands. Monodispersed Ni nanoparticles with average size of 45 nm were prepared using the complex of nickel formate with oleylamine ligands.

Keywords: Nickel, Nanoparticles, Nickel formate, Magnetic materials, long-chain amine

Introduction

Metal nanoparticles having special properties, which are unavailable with bulk materials, have attracted a great deal of interest in recent years. Nanoparticles of transition or noble metals such as Co, Fe, Ni, Cu, Ag, and Au have been extensively studied for use as catalysts, photonics, electronic and magnetic devices. Among these metals, Ni nanoparticles have attracted much attention in application to conductive adhesives and electrodes in multilayer ceramic capacitors, because of low cost over silver nanoparticles and better chemical stability compared to copper nanoparticles. Recently, unaggolomerated pure Ni nanoparticles for technological applications are required to have fine particle sizes between 50 - 100 nm with narrow size distribution as well as high crystallinity, because nanoparticles with the sizes below 20 nm suffer from low oxidation resistance.

Until now, Ni nanoparticles have been prepared by various chemical reduction methods using strong reducing agents such as hydrazine¹ and sodium borohydride². A new process is desired for preparation of pure Ni nanoparticles and the microwave technique is a promising alternative for such methods.

The pyrolysis of nickel formate salts gave pure Ni nanoparticles having sizes between submicro and micrometer at 573 K³. However, the reaction of the heterogeneous dispersion of insoluble nickel formate dihydrate induced aggolomeration of the resulting particles. We have succeeded in preparation of fcc Ni nanoparticles by the reduction of Ni²⁺ ion contained in its formate complex with the long-chain amine ligands under microwave irradiation. The particle sizes were controlled between 50 -100 nm using several long-chain amine ligands.

Experimental details

Nickel formate dihydrate (5 mmol) and oleylamine (30 mmol) were mixed, and then heated at 393 K for 10 minutes. Tetraethylene glycol dimethyl ether (60 ml) was added to the solution. This solution in a quartz vessel was heated with a multi-mode 2.45 GHz microwave apparatus μ Reactor

(Shikoku Instrumentation Co., Ltd) at 770 W at a rate of temperature increase of 40 K / min, and then kept at 463 K for 10 min under nitrogen atmosphere. The temperatures of the reaction solution were measured with a fiber-optic thermometer (AMOTH TM-5886, Anritsu Meter Co., Ltd.) directly inserted into the solution. The Black Ni nanoparticles were rapidly obtained by microwave heating at 463 K (denoted as **A**).

Results and discussion

1) Structural characterization

The crystal phase of the powder was analyzed with powder X-ray diffraction (XRD) with a Cu-K α radiation source with a MultiFlex (Riagaku Co.). The XRD patterns of sample **A** corresponded to the pure phase of fcc Ni, and showed high crystallinity (Figure 1). The size and morphology were characterized by a transmission electron microscopy (TEM) at 200 kV with a Hitachi H-800 (Hitachi High-Technologies Co.). The TEM image of sample A is shown in Figure 2. The average particle size of sample **A** was about 45 nm. In addition, we have achieved control of the particle sizes by changing chain length of the alkyl amine under the same reaction conditions.

2) Difference in Ni nanoparticles between microwave-assisted and conventional methods

In the case of conventional heating, Ni nanoparticles were prepared in the same reaction conditions except for the heating rate (denoted as sample **B**). The reaction solution was heated at a rate of temperature increase of ca. 5 K / min in an oil bath. Larger agglomerated particles among the particles of sample **B** were observed from TEM images than those obtained under microwave irradiation. In the microwave-assisted method, the reaction solution was quickly and uniformly heated under microwave irradiation. Therefore, nucleus growth simultaneously should occur in a whole vessel and the particles with narrow size distribution should be obtained within a short time.

Conclusion

We have succeeded in rapid preparation of monodisperesed Ni nanoparticles by the reduction of Ni^{2+} ion contained in its formate complex with the long-chain amine ligands under microwave irradiation. A long-chain amine ligand attached to the Ni^{2+} complex promoted the reduction of Ni^{2+} ion and enabled control of the particle sizes of Ni nanoparticles.

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Fig. 1. XRD patterns of sample A.



Fig. 2. TEM images of samples A (a) and B (b).

MORPHOLOGY-CONTROLLED GROWTH OF ZnO NANOSTRUCTURES USING MICROWAVE IRRADIATION : FROM BASIC TO COMPLEX STRUCTURES

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ABSTRACT

Morphology-controlled growth of ZnO nano- and microstructures was achieved by microwave irradiation. Various basic ZnO structures, including nanorods, nanocandles, nanonedles, nanodisks, nanonuts, microstars, microUFOs and microballs were synthesized at a low temperature (90 °C) with low power microwave-assisted heating (about 50 W) and a subsequent aging process. These results could be obtained by changing the precursor chemicals, the capping agents, and the aging times. More complex ZnO structures, including ZnO bulky stars, cakes, and jellyfishes, were constructed by microwave irradiation to a mixture of the as-prepared basic ZnO structures and the solution , or . This is a fast, simple and reproducible method which does not require any template, catalyst or surfactant, but can control the morphology of ZnO crystals from simple to complex. Scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy dispersive X-ray spectroscopy (EDX), and X-ray diffraction (XRD) were used to observe the morphology, crystallinity, and chemical composition of the ZnO structures. A growth mechanism for shape-selective ZnO synthesis was proposed based on these results.

KEYWORDS: Zinc oxide, Nanostructure, Morphology control, Seed crystal, Microwaves

INTRODUCTION

The properties of ZnO are strongly dependent on its structures, including the morphology, aspect ratio, size, orientation and density of crystal. These structural characteristics have an important role in many optoelectronic applications. Therefore, development of a shape-controlled ZnO synthesis method is indispensable for exploring the potential of ZnO as smart and functional materials.

In this paper, we report a novel chemical method to synthesize ZnO crystals from basic to complex structures using a fast, simple and low-temperature microwave irradiation method. Our method works at a low temperature (90 $^{\circ}$ C) with a low microwave irradiation power (about 50 W) and has a short reaction time (15 min). It does not require any template or catalyst. Details of the experimental procedures are given elsewhere.

RESULTS AND DISCUSSIONS

The morphological variation of ZnO structures is achieved by controlling the crystal growth and dissolution rates in specific directions and the concentration of ZnO growth units. **Figure 1** shows FESEM and TEM images of the basic ZnO structures with different morphologies. ZnO nanorods can be clearly observed in figure 1(a). These rod-like structures have an average diameter of about 250 nm and an average length of about 1.5 μ m. Figure 1(c) displays ZnO needles which have a diameter of about 100 nm in the middle and a length of about 1.5 μ m. These nanostructures have sharp tips with smaller diameter than that of the middle. The aspect ratio of ZnO needles is higher than that of ZnO rods. ZnO candles, crystal structures with a cavity at the end, can be observed in the SEM image in figure 1(e). The TEM image, shown in figure 1(f), shows the wall of these cavity

structures is thinner at the end. The average outer and inner diameters of the cavity of ZnO candles are about 170 and 100 nm, respectively. The average length of these structures is about $1.2 \mu m$.

The atomic structures of ZnO structures were characterized by high-resolution transmission electron microscopy (HRTEM). The HRTEM images in the insets of Figure 1(b), (d) and (f) show that ZnO rods, candles and needles are highly crystalline, with a lattice spacing of about 0.26 nm, corresponding to the distance between the (0002) planes in the ZnO crystal lattice. Also, the selected-area electron diffraction (SAED) patterns of the three ZnO structures (insets of figures 1(b), (d) and (f)) confirm that they have crystalline growth along the [0001] direction.

In addition to the above one-dimensional (1D) ZnO nanostructures, we could also achieve morphology control of ZnO structures to give ZnO hexagonal disks, nuts, stars, UFOs, and balls. The average diameter and thickness of the nanodisks, as shown in figure 1(g), are about 600 nm and 200 nm, respectively. These hexagonal ZnO disks are highly crystalline, with a lattice spacing of about 0.28 nm, which corresponds to the interspacing of the $(10\overline{1}0)$ planes, as seen in the inset of figure 1(h). Figures 1(i) and (j) display ZnO nanodisks with holes of about 150 nm in diameter in their center. The TEM image in figure 1(j) shows that the hole goes through the entire thickness. These nut-shaped ZnO structures are also crystalline, with about 0.28 nm between adjacent lattice planes, corresponding to the interplanar spacing of $(10\overline{1}0)$ planes in the ZnO crystal lattice like the nanodisk case.

In figure 1(k), ZnO stars have many spines which grew radially from the center. The average length of each spine is about 5 μ m. Most of these spines have terraces and steps, as shown in the lower inset of figure 1(k). The diameter of each spine varies from about 100 nm at the tip to about 1 μ m near the center of the stars; from this we can suggest that these ZnO structures were synthesized by the layer-by-layer growth mechanism. As shown in figure 1(1), each highly crystalline spine of the ZnO star has a lattice spacing of about 0.26 nm, corresponding to the interspacing of the (0002) planes. Figure 1(m) shows the UFO-shaped ZnO crystals, with a small and rough canopy and a large and smooth fuselage. The average diameter and thickness of these structures are about 1.3 μ m and 700 nm, respectively. Spherical ZnO crystals with diameters of about 1.3 μ m are displayed in the SEM image of figure 1(o). The HRTEM images in the inset of figure 1(n) and (p) show that highly crystalline ZnO UFOs and balls have a lattice spacing of about 0.28 nm, which corresponds to the distance between the (1010) planes in the ZnO crystal lattice.

Figure 2 shows a schematic diagram of the proposed formation mechanisms of basic ZnO structures. The ZnO crystal structures can be described as the hexagonal close packing of oxygen and zinc atoms. They mainly exhibit several crystal planes: a top tetrahedron corner-exposed polar zinc (0001) face, six symmetric nonpolar $(10\overline{1}0)$ planes parallel to the [0001] direction and a basal polar oxygen $(000\overline{1})$ face. Each plane group has the different polarity. When ZnO nuclei are formed in the initial growth stage of crystals, ZnO crystals grow preferentially along the [0001] direction. As the reaction goes on, the dissolution effect becomes more prominent owing to the reduction of the concentration of growth units. Therefore, the end of a rod becomes flat as seen in figure 1(a) and (b). The capping effect plays a key role in our morphology control. Detail mechanism can be found elsewhere.

ACKNOWLEDGEMENT

The authors would like to thank the Ministry of Education of Korea for its financial support through the second phase BK21 program. This research was also supported by the Korea Foundation for International Cooperation of Science & Technology (KICOS) through a grant provided by the Korean Ministry of Science & Technology (MOST) in NANO/BIO /INFO Technology (NBIT) Symbiosis.

Figure 1. The basic ZnO structures synthesized by the microwave irradiation. (a) and (b) Nanorods (from solution I). (c) and (d) Nanoneedles (from solution II). (e) and (f) Nanocandles (from solution I and aged). (g) and (h) Nanodisks (from solution III). (i) and (j) Nanonuts (from solution III and aged). (k) and (l) Microstars (from solution IV). (m) and (n) MicroUFOs (from solution V). (o) and (p) Microballs (from solution VI).



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Figure 2. Schematic diagram of the proposed formation processes of the basic ZnO structures. (a) Nanorods or Nanocandles. (b) Nanoneedles. (c) Nanodisks or Nanonuts. (d) Microstars. (e) MicroUFOs. (f) Microballs.



Microwave Assisted Gel Combustion synthesis of Nanocrystalline α-Alumina

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Abstract

Nano crystalline alpha alumina powder was synthesised by a Microwave Assisted Combustion synthesis using citric acid and aluminum nitrate as precursors. The thermal decomposition of the precursor and subsequent formation of α alumina was investigated by X-ray diffraction (XRD), Fourier transform infrared spectra (FTIR), Transmission electron microscopy (TEM) and Thermogravimetry-differential thermal analysis(TGDTA) and BET surface area. The single phase α Alumina could be achieved at a calcinations temperature of 1000 ⁰C. Further, the citrate to nitrate ratio of 0.833 was found to be ideal resulting in well dispersed nano particle with crystallite sizes in the range of 80-100 nm.

Keywords : Gel combustion, Microwave, Nanoparticles

1. Introduction

In recent years, there has been an increasing interest in the synthesis of nanocrystalline metal oxides due to important applications in advanced ceramics and an reinforcement in polymer and brittle matrix composites and other applications. Various chemical methods are employed for the synthesis of alpha alumina such as spray pyrolysis, sol-gel process, precipitation, vapour phase reaction, hydrothermal and combustion synthesis. Combustion synthesis is particularly a simple, safe and rapid production process wherein the main advantages are energy and time savings. This quick, straight forward process can be used to synthesize homogeneous, high purity crystalline oxide ceramic powders with broad range of sizes¹.

Microwave synthesis of ceramics has been the focus of attention of many researchers in recent years². The effectiveness of using microwaves for drying, calcination, binder removal etc. have been demonstrated in laboratories throughout the world and some processes have found to become an industrial reality. Microwave processing can offer advantages over conventional firing methods including uniform heating, less processing time and energy savings.

The α alumina was synthesised by combustion using different fuels viz. urea³, glycine⁴, citric acid⁵ using conventional processing method with Aluminum Nitrate as the oxidant in all the cases. Further, few reports are also available on the combustion synthesis of this material using microwave energy⁶ with urea as a fuel and aluminum nitrate as the oxidant. It was noted from all these studies that citric acid is a suitable fuel in producing the fine alumina powder. The effect of microwave energy on this fuel for producing alumina has not been reported. In this work the microwave assisted combustion synthesis of alpha alumina using citrate and nitrate as the precursors was carried out.

2. Experimental Procedure

The main raw materials used for this experiment were laboratory reagent grade of extra pure $Al(NO_3)_3.9H_2O$ (M/s S. D. Fine Chemicals, Mumbai, India) and Citric acid $C_6H_8O_7.H_2O$ (M/s S. D. Fine Chemicals, Mumbai, India) as the oxidant and the fuel respectively. The initial

INFLUENCE OF MINERALOGY AND TEXTURE ON MICROWAVE-INDUCED WEAKENING OF ORES

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ABSTRACT

Fundamental understanding of microwave-induced ore weakening is leading towards industrial implementation of this technology. Thermal, mechanical and dielectric properties of constituent minerals give rise to weakening when exposed to high electric field strength microwave radiation. Many ores exploited for their metal content contain sulphide and oxide minerals which can be heated rapidly using microwave energy. Subsequent thermal expansion results in stresses that generate micro-fractures. Micro-fractures result in a reduction in the mechanical energy required to crush and grind the ore to a size where downstream separation processes are conducted most Numerical modelling work previously published by the research team showed efficiently. microwave-induced strength reductions correlated well with published experimental results. The modelling work yielded insights as to the influence of the mechanical properties of constituent minerals on the degree of weakening. Fracturing has been shown to be optimised when temporal and spatial thermal gradients are maximised. The work presented here examines the influence of mineralogy, texture and microwave energy input on the degree of fracture generation in a Cu/Ni ore and a Cu ore.

INTRODUCTION

Comminution or rock breakage, accounts for 30-70% of the power draw of a typical mineral processing plant and for 20-50% of the capital cost [1]. It is thought that as much as 3% of the electrical energy generated in the US and as much as 5% globally is consumed by comminution [2] in the mining and minerals processing industry. However the comminution process may be less than 1% efficient in terms of the energy required to generate new surfaces, as much of the energy imparted by the mill for example result in events that do not result in breakage [1]. Microwave technology has been identified as one of two technologies that offer the potential for step change improvements in efficiency. Ores are made up of minerals which show wide variations in their dielectric properties [3, 4]. The bulk of most rocks are made up of various silicate and carbonate minerals, which are predominantly transparent to microwave radiation. However, many metal oxide and sulfide minerals found in ores exploited for their metal content can be heated at rates exceeding 1000°C/s under certain conditions. These minerals expand according to their thermal expansion coefficients, and generate stresses that can exceed the strength of the rock [5].

The ultimate aim of comminution is to reduce the size of ore particles to such a degree that they eventually consist predominantly of individual phases, which can then be separated by chemical or physical means from the remainder, also known as gangue [1]. As the size of particles is reduced, the degree of liberation of the constituent minerals increases. The degree of liberation is a key indicator of ore processing efficiency as it describes the available area of mineral grains (valuable or otherwise) that are available for physico-chemical separation processes such as flotation or leaching.

PREVIOUS EXPERIMENTAL AND NUMERICAL MODELLING WORK

Strength reductions and enhanced liberation have been reported for microwave treated ores by Kingman et al [6] and the mechanisms described numerically by Jones et al, [7,8]. There should

be an optimal proportion of absorbent minerals with the remainder being transparent to microwave radiation, and this ensures that there is sufficient power density within the microwave-absorbent grains to experience thermal expansions of sufficient magnitude to generate levels of adequate stress for fracture. Minerals exhibiting large thermal expansion coefficients will perform favourably. Pentlandite, a valuable nickel sulphide mineral, can exhibit a large thermal expansion coefficient, 206x10⁻⁶ [9], whilst calcite shows a thermal expansion coefficient which is very low at 3.8×10^{-6} [10]. In essence, the numerical modelling papers have demonstrated that effective breakage occurs when thermal gradients are maximised. This occurs temporally when the rate of temperature rise over time is high, and spatially when there are large differences in microwave absorbance either side of a grain boundary. Subsequent work on the same model has shown that breakage and liberation should be enhanced if the matrix phase is particularly stiff, thus allowing for the effective transmission of stress. Some minerals, such as pyroxene and hematite have relatively high bulk and shear moduli and allow for the effective transmission of stress generated from microwave-induced thermal expansion. Certain sheet-silicate minerals such as talc, biotite and muscovite have low bulk and shear moduli and are considered to be soft and as such may yield when impinged upon by expansive species.

MINERALOGICAL AND TEXTURAL ANALYSIS

The mineralogy and texture of two ores have been evaluated using a Mineral Liberation Analyser which captures images of polished ore samples, and uses energy-dispersive X-ray analysis to determine the composition of phases with different gray-scale levels. This allows the characterisation of the ore in terms of absorbent and transparent minerals and whether the absorbent minerals occur in grains large enough to result in sufficient magnitude of expansion to cause significant stress, and also whether those absorbent minerals are associated with a phase which is hard or soft. Examples of ore textures are presented below in Figure 1. Note that each pair of images represents the modal mineralogy of the ore particle in the top image, and below the subsequent grouping of minerals based on their microwave-absorbent characteristics.



Figure 1: Example textures of Cu/Ni ore (left) and Cu ore (right)

The texture on the left shows a copper-nickel ore, predominantly consisting plagioclase and pyroxene. The sulfides (numbered 1-3) pentlandite, pyrrhotite and chalcopyrite, have been grouped as absorbent minerals, and can be seen to be relatively abundant, making up over 8% of the mass, and occurring in relatively large grains. The remainder (apart from 1.5% magnetite) can be

considered microwave transparent. Pyroxene and plagioclase can both be considered as having relatively high bulk and shear moduli, and therefore allow for the effective transmission of stress. The texture on the right shows a copper/molybdenum ore. The microwave-absorbent minerals (numbered 1-6) are relatively scarce, and are considerably finer than those seen in the copper-nickel ore. As such, they may not occur in grains considered large enough to generate significant stresses after microwave treatment. Furthermore, the particle contains a significant proportion of muscovite that is considered soft, and may yield when impinged upon by expansive minerals. Similarly, it contains numerous voids, which again may hinder brittle fracture.

PRE AND POST-MICROWAVE TREATMENT MECHANICAL TESTING

The breakage characteristics have been evaluated before and after microwave treatment using non-destructive Ultrasonic Pulse Velocity (UPV) measurements. UPV decreases as micro-fractures are introduced, which lengthen the transit path. Particles of ore were prepared by cutting into regularly-shaped cuboids of approximately 20-25mm diameter with the aid of diamond-impregnated saws in order to minimise variability arising from shape effects. The dimensions of each particle were measured using vernier callipers, and were then subjected to UPV measurements in numerous locations across the particle face. Particle sets were then subjected to microwave treatment in a WR430 TE_{10n} single mode cavity, using a 30kW 2.45GHz microwave This methodology was previously documented in the paper by Kingman et al, 2004. generator. Treatments were carried out at two treatment times for each ore, so that the influence of varying energy input could be evaluated. The behaviours of the ores are shown in エラー! 参照元が見 whereby the percentage change in UPV after microwave treatment for each ore つかりません。 and treatment condition is plotted for each particle measurement in ascending order from left to right.



エラー!参照元が見つかり ません。 shows that for both ores, the percentage reduction UPV in increases with increasing energy input. It is clear that the Cu/Ni ore is damaged to a greater degree than the Cu ore. The Cu/Ni ore treated at 0.7kW.h/t outperforms the Cu ore treated at 7.7kW.h/t. The improved performance of Cu/Ni is likely to be due to the greater incidence of microwave absorbent minerals, the higher average absorbent grain size,

Figure 2: Spread of % change in UPV for MW-treated ore

and the relative stiffness of the non-microwave-absorbent minerals. The Cu ore only exhibits modest improvements due to the relative scarcity of microwave-absorbent minerals, the low average grain size, and the presence of muscovite and voids which hinder the effective transmission of stress.

Particles of the Cu/Ni ore were examined using the SEM, before and after treatment, to determine whether any cracks generated as a result of treatment could be observed. The micrographs in Figure 3 show the particle before and after treatment. Note the incidence of cracks running along numerous grain boundaries. There were no instances whereby fractures were observed in the Cu

ore after treatment. Any reductions in ultrasonic pulse velocity observed may have occurred due to the generation of cracks too small to observe using the SEM.



Figure 3: Micrographs of Cu/Ni ore before (left) and after MW treatments showing intergranular fracture

CONCLUSIONS

The evaluation of mineralogy and texture can be used to aid explanation of the degree to which ores are affected by microwave treatment. Mineralogical analysis allows the characterisation on the basis of the proportion of microwave absorbent minerals and microwave-transparent minerals. Similarly it allows the characterisation of the mechanical properties of the ore on a per-mineral basis. Textural evaluation shows whether absorbent minerals occur in grains sufficiently large that their expansion generates fractures. It has been shown that microwave-induced thermal stress generation will be most effective for ores that contain an optimal amount of highly microwave-absorbent, thermally-expansive minerals, in a predominantly microwave-transparent matrix of high bulk and shear modulus.

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INCREASED COAL GRINDABILITY AS A RESULT OF MICROWAVE TREATMENT AT ECONOMIC ENERGY INPUTS

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ABSTRACT

This paper will show how microwave energy can be used to increase coal grindability by around 40% for most coals, measured in terms of specific rate of breakage. High power microwave treatment (9kW) of coals for very short residence times (0.1 s) can produce physical changes, such as cracks and fissures, in coal particles both on the surface and inside the particle across a wide size range. These cracks are responsible for the observable differences in grindability during ball milling. The energy input by means of microwave treatment equals 0.44kWhr/t, which is about 3% of the total energy required for mills to meet the fineness requirement. Considering that the average improvement in breakage is 38% for 16 seconds and 29% for 32 seconds in ball mill, there is great potential to reduce energy requirement for milling. The results for larger scale trials (ton scale) will demonstrate how economic saving can be realised using high power, low residence treatments for coal and how this technology might scale up for industrial implementation.

INTRODUCTION

The energy consumption of the grinding mills in a coal fired power plant is significant. A company would immediately benefit if this energy requirement could either be reduced or used to create a finer product. The IEA has forecast that 38% of the world's electricity will still be generated from coal by 2030 [1], so it is imperative that higher energy efficiencies are achieved as part of the drive towards worldwide sustainability.

A significant improvement in coal grindability would obviously allow the power requirement to the mills to be reduced. More importantly it would also allow the throughput to the burners to be increased, or a smaller grind size used, depending on the operational requirements of the station at any given time. Since a single MWhr sells for £15 to £20 on the UK energy market, reducing coal grinding resistance would produce significant financial savings in addition to potentially reducing carbon dioxide production. For example, if the energy required to grind a coal to 70% less than 75 microns can be reduced by up to 30-50% through some pre-treatment technique which utilises a much lower energy consumption, the economic returns could be measured in millions of pounds.

Within the grinding process achieving a size of 70% less than 75 microns is important since oversize particles inevitably cause burnout problems [2] even when the coals are highly volatile[3]. A finer grind at no extra milling cost would enable power companies to obtain lower levels of carbon in their flyash [4]. The energy required to grind a standard bituminous steam coal to pf for a 500 MWhr power generation unit at full load is 3.6 MW (including PA fan) [5], which equals to about 18kWh/ton coal.

Preheating a coal in a traditional oven has been shown to reduce grinding resistance, although it is unlikely that this would be an economically viable method, not least through associated energy requirements[6]. Microwave heating is fundamentally different from conventional heating since microwaves take the form of electromagnetic energy and can penetrate deep in the sample allowing volumetric heating. Conventional thermal processing will heat the sample from the outside through standard heat transfer mechanisms i.e. through convection, conduction and radiation, and this will inevitably require time. In addition, extended heating may produce undesirable effects on the sample itself e.g. oxidation, hence making conventional heating an unattractive option.

There is evidence in the literature of how microwave treatment can significantly reduce the strength and therefore improve the grindability of coal particles[7-9]. Recent work utilising low power domestic type microwave ovens showed that up to 50% increases in grindability in UK coals could be produced as a result of microwave treatment. The authors conclude however, that whilst the benefits of treatment were technically attractive the economics were poor with much more energy being added to the process than could be potentially saved.

Previous work at The University of Nottingham [10] has shown that coal (in particular, the inherent moisture) responds well to microwaves and that the grindability can be significantly enhanced as a result of microwave treatment. Recent work by the authors has shown that by maximisation of microwave power density (volumetric heating rate) and reduction in cavity residence time, significant process benefits, including reduced comminution energy at microwave energy inputs of less than 1 kWht-1 can be achieved [11, 12]. For the first time it may be possible to significant reduce the required grinding energy of coal at economic microwave energy inputs and industrially relevant throughputs. The key to this is the ability to design cavity systems which generate targeted high electric field strengths responsible for ultra rapid heating and the development of high power pulsed microwave generators which require relatively low total power but give very high peak power outputs for very short durations.

EXPERIMENTAL

The chosen coals were supplied by power stations in order to keep the project directly relevant to industry. Three coals were chosen for testing, Daw Mill, Indonesian and La Loma. Upon receiving all coals were air dried for 24 hours in the laboratory to remove part of the surface moisture and therefore improve the handleability and ease and accuracy of bulk sampling in laboratory. Table 1 shows the proximate analysis data for each coal. As observed in a previous investigation [11], microwave treatment tends to have a more significant impact on larger size fractions (>10mm) with less impact on smaller size fractions (<10mm). However, this observation is also related to coal moisture content and the form of moisture present within the coal. In this project, size analysis was carried out on all coal samples on an as-received basis. To investigate the influence of size effects on grinding behaviour, coal samples were sieved into 3 size fractions, namely, +4.75-6.70mm, +9.50-13.20mm, +13.20-19.0mm, with larger lumps in the 'as received' samples being jaw-crushed. All sieved coal size fractions were representatively split into two portions, one for a ball-mill grindability test and another one for microwave treatment prior to an identical ball mill grindability test.

	Proximate Analysis (air dried) wt%				Dry ash fi	Fuel	
Coal	Moisture	Volatiles	Fixed Carbon	Ash	Volatiles	Fixed Carbon	Ratio
Daw Mill	2.8	36.3	51.9	9.0	41.2	58.8	1.43
La Loma	3.8	36.8	50.0	9.4	42.4	57.6	1.36
Indonesian	5.7	45.0	47.8	1.6	48.5	51.5	1.06

Table 1. Coal proximate analysis data

Microwave-treatment

0.5kg samples of the three different coals in different size ranges were treated using a TE010 single mode microwave cavity which was capable of operating at powers ranging between 3 to 15 kW and at a frequency of 2.45GHz. This type of cavity was chosen as it has previously been shown as suitable for inducement of the high electric fields required for the generation of thermal stresses of a magnitude above that required for coal breakage. The residence time of the coal sample within the microwave field was varied by moving the coal sample (in a 75mm ID glass cylinder) through the microwave field by use of a pneumatic ram. The test apparatus is detailed in Figure 1.

Larger scale trials have been conducted using a continuous tunnel applicator with a microwave generator capable of delivering 3-30kW at a frequency of 2.45 GHz. Residence time is controlled by varying belt speed through the cavity



Figure 1 –Single mode TEM cavity with a coal charge dropping through at a controlled speed.

Grindability Tests

In this project, a relative measure of coal grindability was used for the assessment of grinding behaviour using a ball-mill. Comparative specific rate of breakage Ball-mill tests (25cm diameter Bico-Braun Laboratory Ball Mill) were performed extensively in this project to compare the change in grindability of individual untreated and treated size fractions. The ball mill test consists of taking a closely sized fraction of material and grinding for a set time or number of revolutions. The sample is then screened at the bottom size of the original size fraction and the mass left in the original fraction determined. If mass left in the original fraction is then plotted for a range of increasing grinding times the specific rate of breakage of the particles can be calculated and the rate of decrease in mass observed. Whilst this value is not an absolute determination of energy consumption it does allow the relative change in grindability as a result of microwave treatment to be determined. From the data the rate of fracture utilisation can also be determined by plotting the breakage rate based on discrete time intervals (slope between two discrete time intervals) versus total grinding time. By comparing the values for treated and untreated coal with time it can be seen that when the values for an individual size fraction are similar then the cracks induced as a result of the microwave treatment have all been utilised. This is because the presence of microwave induced flaws gives rise to a greater rate of breakage in the treated fraction.

RESULTS

Table 2 shows the specific rate of breakage against time elapsed in ball mill for the coal ground in the mill with the reduced charge. It is clear that La Loma coal responds well to microwave treatment with an increase of 580% in specific rate of breakage observed for the +9.50-13.20mm size fraction of La Loma coal.

Coal Origin	Size	8 s	16 s	32 s	50 s	100 s	150 s
Daw Mill	+16.00-19.00	48%	46%	43%	20%	31%	19%
	+9.50-13.20	61%	85%	37%	35%	26%	35%
	+4.75-6.70	29%	18%	14%	29%	35%	35%
La Loma	+16.00-19.00	156%	51%	90%	82%	57%	39%
	+9.50-13.20	580%	343%	209%	173%	81%	84%

	+4.75-6.70	41%	24%	26%	29%	34%	31%
Indonesian	+16.00-19.00	53%	23%	13%	14%	12%	18%
	+9.50-13.20	81%	51%	34%	23%	30%	24%
	+4.75-6.70	12%	8%	9%	10%	4%	7%

Table 2. Improvements in the specific rate of breakage in ball mill

Results of larger scale continuous trials and grindability data will also be presented in the complete paper.

CONCLUSIONS

It was found that coal with inherent moisture within the range of 1.0%-3.5% seems to respond well with microwave treatment. It has been found that an average of 69%, 38% and 29% improvement in terms of specific breakage of rate for milling for 8s, 16s and 32s respectively in the ball mill have been achieved. This suggests great potential for energy saving in power station grinding since the microwave energy input was as low as 0.5kWhr/t.

The project has shown conclusively that increasing the electric field strength increases the damage induced in the coal structure. High power densities produce a pressure increment across each coal particle that is significantly greater than the rate of escape of the resultant steam. If the sample is heated slowly the rate of escape is greater than the pressure rise and no fractures occur. High power densities and low exposure times are the key to success in fracturing coal.

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MICROWAVE SINTERING OF ALUMINUM ALLOYS

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ABSTRACT

Until 2000 almost all research in the microwave sintering area was confined to non-metallic materials. However, after the first report by Penn State in 1999¹ on full sintering of steel powders in microwave, now in the last few years there has been increasing interest in applying microwave energy for processing of variety of metallic materials. The present study is an extension of this work and relates to the sintering behavior of aluminum alloy powders. Blended 2712 (Al-Cu-Mg-Si-Sn) and 6711 (Al-Mg-Si-Cu) alloy powders were consolidated by microwave sintering through temperature range of 570 to 630 °C for 1 hr in vacuum, nitrogen, argon and hydrogen atmospheres. The influence of sintering temperature and atmosphere on densification response were investigated in comparison with conventional sintered parts. Microwave sintering enhanced the densification response in shorter times and lower sintering temperature in turn leading to better properties.

Keywords: P/M Al alloys; microwave sintering, vacuum atmosphere, phase analysis, swelling.

INTRODUCTION

The application of P/M aluminum alloys has been increasingly used in automotive industry, where low cost and light weight materials are the essential design criteria. The P/M aluminum alloys are replacing small AI die casting which requires precision net shaping and better material utilization [1]. Sintering of aluminum alloys were considered to be very difficult due to the presence of the thermodynamically stable oxide layer on powder particle surface, which required an oxygen partial pressure of $<10^{-50}$ atm at 600°C to be reduced [2]. However, it has been demonstrated that nearly full density can be obtained by the newly emerging technology of microwave sintering due to its inherent uniqueness and advantages [3]. Microwave heating has several advantages over conventional sintering process such as rapid heating rates, short cycle time, improved product quality and environmentally friendly [4]. Microwave sintering has been extensively used for consolidation of ceramics and hard metals, until Roy et.al [4] for the first time showed effective coupling of microwaves and metals in powder form. Later on many researchers have reported microwave sintering of many powdered metal compacts and alloy compositions (steel, stainless steel, Cu, Al, Ni, Ni, Mo, Co, Ti, W, WC, Sn etc) to nearly full dense bodies in turn better properties [5-14]. W. Wong et.al [15] have reported the two-directional heating for sintering of materials like Mg, Al and lead free solder for short time. In the present work, an attempt has been made for effective sintering to take place by combining protective atmosphere and novel microwave sintering technique has been employed for improving densification and properties.

EXPERIMENTAL DETAILS

The prealloyed 6711 and 2712 Al alloy powders with particle size $[d_{50} = 83.58$ and $d_{50} = 104.75]$ respectively was supplied by AMPAL Inc., U.S.A. The typical SEM micrograph of aluminum alloy powder resulted in spherical morphology as it was processed by gas atomization process as shown in Fig.1a. The alloy powders were compacted at 200MPa using a uniaxial press (model: CTM-50; supplier: FIE, Icharanji, India) to cylindrical pellets (diameter: 16 mm and height: 6 mm to green densities of 96.42 ± 0.97. Before sintering, delubrication was carried out in conventional vacuum furnace at 350°C for 6hrs in vacuum range of 10^{-2} to 10^{-3} Torr. The microwave sintering was carried out using 2.54Hz, 6kW multimode furnace in vacuum, nitrogen, argon and hydrogen, respectively at temperature ranging from 570 to 630 °C for 1 hr. Conventional sintering of green compacts were carried out in a SiC heated horizontal tubular sintering furnace (model: OKAY 70T-7, supplier: Bysakh, Kolkata, India) at constant heating rate of 5°C/min at above mentioned atmosphere and temperatures. The thermal cycle profiles for microwave and conventional sintering of aluminum alloy is shown in Fig.1b. The sintered densities of samples were measured using Archimedes' method. The densification parameter (D.P) is expressed as in equation (1):

$$D.P = \frac{(s \text{ intered density - green density})}{(theoretical density - green density)}$$
(1).

The TGA analysis was carried on the green compacts before and after delubrication at 10°C/min in nitrogen atmosphere at 700°C, which shows the complete removal of lubricant as shown in Fig.1(c).



Fig.1 (a) SEM of typical Al alloy powder (b) Thermal cycle for microwave and conventional sintering of Al alloy (c) TGA analysis of Al alloy compact before and after delubrication.

RESUTLS AND DISCUSSION

Fig 2(a) shows the densification response of conventional and microwave sintered samples of Al-3.8Cu-1Mg-0.8Si-0.3Sn (2712) alloy. It can be seen that sintered density increases with sintering temperatures

for all cases in microwave in vacuum atmosphere as compared with conventional parts. The vacuum sintering normally produces higher densities, since sintered alloy does not emit any vapor to fill pores or no decomposition occurs, and the densification happens by unimpeded trapped gases [16]. Vacuum sintered are hypothesized to have closed pores and less porosity which can be confirmed on further metallography investigations.

The higher sintered density was observed for microwave nitrogen sintered samples at 590°C and thereafter a decreasing trend, whereas conventional samples resulted in better densification at higher temperatures (630°C). At lower sintering temperature, Al-Cu alloys experiences either swelling or shrinkage behavior. The higher sintering temperature results in initial swelling; followed by shrinkage such that alloy attains the solid-liquid state region [17]. It can be seen that microwave sintered samples in N₂ decrease in density after 590°C, due to the faster heating rate during microwave heating, Cu, Mg, Si have less time to diffuse into Al lattice and therefore the spreading of liquid phase reduces causing to slow down the homogenization process[18]. Hence it can be hypothesized that microwave sintering in N₂ at 590°C has attained an alloy homogenization, and contained sufficient volume fraction of permanent liquid.

Conventional and microwave samples sintered in Argon atmosphere showed an increasing trend in density with sintering temperatures, except at 630° C for microwave case. The samples sintered in H₂ also followed similar trend as nitrogen sintered ones, with higher density at 590°C, thereafter decreasing trend in density. The densification parameter was observed to be positive for vacuum sintered samples for conventional mode at 630°C and at temperatures higher than 590°C for microwave mode as shown in Fig.2 (a). Also nitrogen microwave sintered samples at 590°C resulted in slighter swelling as compared to other sintering temperatures and heating mode. The argon and hydrogen sintered samples exhibited more or less the similar swelling behavior slightly higher than nitrogen and vacuum sintered samples in both heating modes.

The swelling behavior of above alloy can be well explained by dilatometric experiments as seen in Fig.3 (a). From the dilatometeric curve for 2712 alloy, initially compacts undergo swelling at lower temperature and therafter additional amounts of liquid formation occurs on melting of Mg particles, dissolution of Cu and Si in liquid, and formation of intermetallics [19]. The maximum swelling started occurring at 510°C; which may be due to the transient liquid formation, followed by diffusing of the alloying elements Cu an Mg into aluminum matrix leaving behind the secondary pores leading to additional compact swelling behavior [16].

Another eutectic reaction occurred at 548°C which is not accompanied by sample swelling, which led to change in slope of dilatometry curve. The shrinkage occurred thereafter due to large amount of liquid phase formation [17]. At higher sintering temperatures (590°C), larger volume fractions of liquid results in enhanced densification. The densification mechanism of vacuum sintered differs from nitrogen sintered samples in case of both heating modes; where densification occurs by pore filling mechanism in later stages of sintering for latter case [2]. The reduced density of argon and hydrogen sintered samples in both heating modes, was mainly due to the presence of entrapped gases inside the pores, leading to inhibition of densification and inferior properties. Microwave sintered 2712 alloy resulted in enhanced densification in vacuum atmosphere followed by nitrogen, argon and hydrogen as compared to conventional.

ENERGY DISSIPATIION IN METAMATERIAL

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ABSTRACT

Metamaterial as artificial material having exceptional electromagnetic properties recently comes up great attention. In particular, metamaterial with both negative permittivity and permeability have attracted widespread interest. Such composites can be constructed from an array of metallic pieces with special shapes. In this paper, heating characteristics are discussed for such metamaterial. Simulated result reveals such new material concept will reveal special heating effects to accelerate chemical reaction and metal powder heating.

Key words: microwave heating, artificial dielectric material, metamaterial, double negative, microwave propagation, energy dissipation

I. INTRODUCTION

Microwave irradiation is recently applied to accelerate chemical reaction. Moreover, recent microwave advanced technology makes it possible to increase electric field (E field) using artificial dielectric material [1], [2] and metamaterial. In this paper, electric field characteristics in the metamaterial is studied. To achieve this objective, simulation of electromagnetic field in the clearance of granular medium, artificial material and metamaterial are performed. Transmission Line Modeling (TLM) method is applied to obtain E-field distribution inside the medium.

II. METHOD

Heating target is simulated to be a granular medium. The granule is considered to be spherical material to be considered as artificial dielectric. Microwave field is externally irradiated to the granular medium. Frequency dependent E-field in the clearance of granules is obtained using TLM method. Simulation setup is shown in Fig. 1. In Fig. 1, the positions to obtain E-field are demonstrated as A, B, C and D. The simulated model is shown in Fig. 2. Next procedure to study



Fig. 1. Simulation setup with the position to obtain electric field.





Fig. 3. Designed periodical metallic structure as metamaterial .

exceptional electromagnetic properties is to apply periodical metallic structure on the substrate. The structure is shown in Figs. 3. The propagation of electromagnetic (EM) waves in the material is simulated.

III. RESULTS

The frequency dependent E-field in the position A, B, C and D in Fig. 1 when the clearance of the metallic sphere d = 1.0 mm is shown in Fig. 4. The frequency dependent E-field in the same position when the clearance of the metallic sphere d = 0.1 mm is shown in Fig. 5. From the results, it is found that in some resonant frequencies, E-field becomes very strong, and the phenomenon as metamaterial occurs around these frequencies. In these frequencies, the E-field distribution in the clearances between the metal becomes high. Such increased E-field in the clearances of the component of the granular structure and metamaterial is shown in Figs. 6 and 7, respectively. The high electric field will cause the discharge and it may accelerate the chemical reaction. Fig. 8 shows the E-field distribution on the surface of the metamaterial. Fig. 9 shows the E-field focus outside of metamaterial. In this case, metamaterial operates such as focusing lens. By such results, high E-field can be easily generated and the focus can be easily made by metamaterial. Also, E-field distribution can be accurately controlled by using the metamaterial structure.

IV. CONCLUSIONS

Electromagnetic field distribution inside the microwave irradiated medium of artificial dielectric materials and metamaterials has been analyzed. The E-field in the clearances of the granular structure and metamaterial component in the artificial dielectric becomes very high in the resonant frequencies. Using such metamaterial structure, the electromagnetic field can be amplified and accurately controlled. The amplification of the E-field in the clearances in the medium of granular structure and the components of metamaterial may cause a chain discharge and the discharge will accelerate the chemical reaction and will be applied to the metal powder rapid heating.

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Fig. 4. Electric field distribution vs. frequency in the medium (d = 1.0 mm).



Fig. 5. Electric field distribution vs. frequency in the medium (d = 0.1 mm).



Fig. 6. Electric field distribution in the granular structure of dielectric material.



Fig. 8. Electric field distribution in the metamaterial.



Fig. 7. Electric field distribution at 2.45 GHz in Metamaterial.



Fig. 9. Electric field focusing outside the DNG metamaterial.

AIR HEATING SYSTEM UTILIZING MICROWAVE SUSCEPTOR CERAMIC MATERIALS

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ABSTRACT

The paper presents the theoretical aspects and experimental data relating to a new, energy efficient air heating system, based on the static accumulation of the heat generated by microwave susceptor ceramic materials and its dynamic discharge (transfer).

The heat source presented in this paper is a new ceramic material that has the property to absorb a high level of microwave energy and convert it into heat.

The microwave susceptor ceramic material, representing the heat source, can generate heat through microwave energy absorption, with temperatures up to 2000 °C, having a good thermal stability at the balance levels between the absorbed microwave energy and absorbed thermal energy (in infrared).

The paper presents the constructive solution and the experimental data obtained for an air heating system utilizing as heat sources the microwave susceptor ceramic materials and as heat accumulating mass – a ceramic material with a high density, transparent to microwave energy, that is heated during heat accumulation and that dynamically yields this heat afterwards through air forced convection.

The experimental data obtained show the heating variation of the microwave susceptor materials for different levels of power in microwave in the form of a plot and the temperature variation of the heat accumulating ceramic mass, in a constructive configuration from which there also results the position of the microwave sources and the forced air circuit ensuring the dynamic discharge (transfer) of the heat accumulated in the accumulating ceramic mass.

At the same time, the experimental data obtained indicate the energy consumption of the new air heating system and makes a comparison with the already known conventional systems utilized at present, pointing out the energy advantages of this new solution.

The final conclusion resulting from the analysis of the obtained experimental data confirms the fact that the heating system presented in this paper is an efficient alternative to the existing heating systems.

KEY WORDS: air heating system, microwave susceptor ceramic material, static accumulation of heat, dynamic discharge of heat.

1. INTRODUCTION

This air heating system is to be utilized in situ within an ecologically integrated multifunctional system for supplying utilities to the dwellings located in the area of the "Danube Delta" Biosphere Reservation from Romania, for the sustainable development of the protected zones of international interest.

A *susceptor* is a material utilized for its property to absorb electromagnetic energy. The name of "susceptor" is derived from "*susceptance*", representing the tendency of the material to convert electromagnetic energy into heat.

Obtaining high temperatures by means of microwave energy is difficult to achieve in the case of most ceramic materials due to the low level of microwave energy absorption at temperatures of up to 500 - 600 ⁰C.

This phenomenon is due to the low value of the loss factor ε " (the imaginary part of the complex dielectric constant $\varepsilon^* = \varepsilon' - j \varepsilon$ ") and especially due to its insignificant increase in temperature of up to 500 – 600 ⁰C values.

The variation of the loss factor ε " with temperature, in the case of most of the ceramic materials [1], underlines the existence of a critical temperature Tc (500 - 600 0 C) from which an exponential increase with temperature in the loss factor occurs, causing an increase in the microwave power level absorbed by the material according to Figure 1.

The analysis of the data presented in literature [1, 2] on the variation of dielectric permittivity ε' and the loss factor ε'' with temperature underlines the fact that, in certain ceramic materials, these parameters present an exponential increase with temperature resulting in the heating of the ceramic with temperatures of up to 2000 - 2200 0 C.

These ceramic materials are included in the category of high microwave absorbing materials, opposite to the microwave transparent materials as concerns their absorption level.

Figure 2 presents the variation with temperature (at the microwave frequency) of the loss factor ε " of two types of susceptor ceramic materials in comparison with other two ceramic materials.



Fig. 1. The variation of the loss factor ε" with temperature in the case of the ceramic materials



Fig. 2. Variation with temperature of the loss factor ε " of the microwave susceptor materials (1, 2) in comparison with other veramic materials (3 – steatite, 4 – porcelain)

The air heating source presented in the paper is made up of a microwave susceptor material. The minimum temperature that the susceptor should develop is of 1200 - 1250 ⁰C, namely the temperature that can heat the air directly or can be stored through static accumulation in a ceramic mass. The microwave susceptor materials that the paper proposes for heating the air, differ in the temperature increase slope and the maximum temperature they develop. Thus:

- The microwave susceptor material A has a temperature increase slope of up to 750 800 0 C, followed by an increase in the microwave energy absorption leading to maximum temperatures of 1100 1150 0 C;
- The microwave susceptor material B has a low temperature increase slope, up to 600 650 $^{\circ}$ C (the microwave absorption level is low), that is continued by a powerful microwave absorption leading to maximum temperatures of 1900 2000 $^{\circ}$ C.

The combination of the two microwave susceptor ceramic materials in different proportions can ensure temperatures of 1200 - 1300 ^oC in a short period of time.

The analyzed variants of the susceptor ceramic parts have the following compositions:

- Variant 1 susceptor material A 80 %, susceptor material B 10 %, the rest are other materials (figure 3)
- Variant 2 susceptor material A 75 %, susceptor material B 15 %, other materials (figure 4)



Fig. 3. Variation of the susceptor ceramic material heating



Fig. 4. Variation of the susceptor ceramic material heating

2. SOLUTIONS PROPOSED FOR UTILIZING MICROWAVE SUSCEPTORS FOR AIR HEATING

2.1. Air heating through forced convection

The forced convection air heater is a closed metallic cylinder containing inside the microwave susceptor pieces that are heated up to 1400 ⁰C and the thermal insulation in the form of a cylinder made up of a ceramic material, as well.

The microwave susceptor ceramic parts are concentrically distributed inside the metallic cylinder and are in the form of a cylinder with holes over its body. A ventilation system ensures the forced air circulation through the microwave susceptor material holes. The air gets heated and is then discharged through the holes located in the superior part of the heater. On the exterior of the closed metallic cylinder spaces have been cut in order to mount wave guides for the microwave sources. Figure 5 schematically presents the air heater with forced convection.



Fig. 5. Diagram of the air convection heater

2.2. Air heater with static heat accumulation

This type of heater is based on the static accumulation of the heat produced by a microwave susceptor in a ceramic mass. The heat stored by the ceramic material can be used afterwards for heating the air in a dwelling place. Schematically, the microwave susceptor assembly – the heat accumulating ceramic mass is presented in figure 6.



Fig. 6. The schematic presentation of the air heating system thorugh heat static accumulation and dynamic discharge: 1 – microwave applicator; 2 – thermal insulation; 3 – heat accumulating material; 4 – microwave sources; 5 – microwave susceptor ceramic material; 6 – ventilator (fan)

3. EXPERIMENTS AND RESULTS

The variation in temperature of the heat accumulating ceramic mass under static accumulation and dynamic discharge operating conditions is given in figures 7 and 8.

In the case of the experiments on the air heating system system with static accumulation and dynamic discharge, the utilized microwave power reaches 1,6 kW at a frequency of 2,45 GHz.







Fig. 8. The curve of the dynamic discharge of the heat accumulated by the ceramic mass

4. CONCLUSIONS

The results obtained experimentally indicate the fact that the solution of microwave susceptor ceramic material utilization for the heating systems with static accumulation and dynamic discharge of heat can be used for heating dwelling places.

Preliminary experimental results have pointed out that its energy consumption is 30 % lower in comparison with other air heating systems.

The air heating systems presented in this paper are also environmentally clean (non-polluting).

The testing of the air heating systems is under way and the results obtained will be analyzed from the point of view of energy efficiency for optimizing it.

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The Development of a 30kW/2450MHz, 500L volume

High Pressure Microwave Chemical Processing System

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Abstract

The development of a 500L volume, 220°C temperature, PH from 3 to 13, 2.5MPa pressure vessel, 30kW/2450MHz, microwave chemical processing system is introduced in this paper. Design and development of the 3 x 10kW/2450MHz microwave power sources, microwave translating and combination system including high pressure sealing windows; specialized microwave reaction vessel and all related key technology, such as controllable mechanical stirrer, input, export and safe guide valves, temperature, pressure and microwave detect sensors all these multiple ports high pressure sealing; high temperature and strong acid alkali resistance operating and microwave power, temperature, pressure sensors and multiple parameters PLC auto control are also presented in the paper. The preliminary application results, further improvement for next larger volume development and its industrial application in the fields of microwave chemical synthesis, decomposition, material modification and assisted extraction are also brief prospected.

KEY WORDS: microwave, chemical, synthesis, processing, system

Introduction

As we all know that microwave chemical processing technology including fast catalyzing synthesis, digestion, assisted extraction and etc. have been rapidly developed and become a new front joint science in recent twenty years and shown an even great wider prospect in the future. With a degree of flexibility and control not found in traditional methods, microwave energy instantly transfers or "couples" to the molecules and ions in a reaction, resulting in instantaneous heating. This

EFFECTS OF MICROWAVE PROCESSING ON POROSITY

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ABSTRACT

One of the primary goals for these studies was to fully understand the effects of the electromagnetic field on porosity so as to control more effectively the microstructures of these ceramic materials. The effect of microwave energy at 2.45GHz was evaluated for two different ceramic materials: fully stabilized zirconia and silica aerogel. In the case of the zirconia, low porosities (< 10% total porosity) were obtained within 20 min of soak time at 1300°C for microwave-processed samples, as compared to 23% total porosity in samples processed conventionally. Isothermal sintering runs performed at 1200°C and 1300°C showed a significant reduction in porosity with soak time in the case of microwave-processed samples as compared to the conventionally processed samples. Monolithic silica aerogel samples were produced by using a sol gel process and dried under critical conditions. These samples received a thermal treatment at ambient pressure in air for 30 min at predetermined temperatures using a conventional furnace and a single mode microwave oven. Differences in pore volume and surface area were observed throughout the thermal process ranging from 600 to 1100°C in both systems.

KEYWORDS: Ceramics, Controlled Porosity, Microstructural Evolution, Sintering, Refractories

INTRODUCTION

The effect of microwave energy at 2.45GHz was evaluated for two different ceramic materials: fully stabilized zirconia and silica aerogel. The primary goal in each case was to understand the effects of the electromagnetic field on porosity so it may be used more extensively in developing ceramic materials with designed microstructures. Numerous reports on the advantages of microwave over conventional heating have been cited in the literature [1-6]. For instance, Janney et al [2] have reported a $100^{\circ} - 150^{\circ}$ C reduction in sintering temperatures. Goldstein et al [4] achieved fully sintered samples (5 mol% yttria-zirconia) using microwave hybrid heating (MHH) at temperatures as low as 1200° C with a 15-20 min dwell time. De' et al [6] have reported enhanced results in density, homogeneity in microstructure, and uniformity in mechanical properties for a MHH sintered Al₂O₃ as compared to a conventionally sintered Al₂O₃. In addition, a substantial reduction of time was reported when compacts of amorphous silica gels were dried using microwaves [8].

EXPERIMENTAL PROCEDURE

Zirconia

Commercially available 8 mol% yttria stabilized zirconia (8YZ¹) powders produced through a hydrolysis process in the form of spray dried granules were used for this study.

Green pellets (or unfired pellets) were fabricated using uniaxial pressing followed by isostatic pressing. Four grams of as-received powder were poured into a uniaxial mold of 12.5 mm diameter

¹ TZ-8Y, Tosoh Corporation, USA

and 70 mm height, and subjected to a pressure of 37 MPa. The pellet formed uniaxially was transferred to isostatic bags and further pressed to 172 MPa. The resulting pellets were cylindrical in shape with a diameter of ~ 11.2 mm and a height of ~ 13.2 mm.

The 8YZ green pellets were sintered at a constant heating rate of ~ 20° C/min using both microwave hybrid and conventional heating techniques. For microwave hybrid heating, a susceptor was made by mixing 2 wt% partially stabilized zirconia with 98 wt% alumina cement. This susceptor absorbed microwaves at a power level of 1500 W and supplies heat to the sample at a rate of 20° C/min to 1200° C. Heating beyond 1200° C was performed by increasing the power level to 2100 W while maintaining a constant heating rate by on/off switching of power. The conventional sintering runs were performed in a high-temperature industrial batch furnace². Temperature measurements for all sintering runs were monitored using an R type thermocouple. A feedback controller maintained a constant heating rate of ~ 20° C/min for all the sintering runs.

<u>Aeorgel</u>

Microstructural evolution in silica aerogel was observed in samples produced by the hydrolysis and polycondensation of acid-catalyzed tetramethylorthosilicate³. Drying of the silica gel was performed using a critical point dryer. After drying, each sample received a thermal treatment in a conventional furnace or in a microwave oven.

The conventional fournace used was similar to the one described before for the 8YZ pellets. The microwave system was a hybrid single mode oven operating at 2.45GHz and using a TE₁₀₃ resonant cavity. A microwave hybrid heating system was used with the silica aerogel due to its extremely low dielectric loss (~ 0.1) at 2.45GHz when it is at room temperature. Basically, microwaves were used to heat up a susceptor material and produce a conventional heating effect on the sample. When the sample increased in temperature, its dielectric loss increased and it became a microwave absorber. In addition, because the distribution of the electric field (*E*) in this cavity was known, the sample was placed in a position where *E* was at a maximum, and the susceptor was in a position where *E* wass lower than that of the sample. In this way, the sample experienced an *E* of larger magnitude and was more likely to absorb higher power.

RESULTS AND DISCUSSION

Zirconia

The results obtained by adopting microwave sintering were compared to those of conventional sintering in Figure 1. It can be observed from Figure 1 that percent open porosity decreased with increasing temperature. Also, microwave processed pellets exhibited a lower porosity when compared to a conventionally processed pellets.

Figure 2 is a plot of porosity vs. soak time at two different temperatures 1200°C and 1300°C. It was observed that, at 1200°C, the microwave-processed pellets showed a drastic decrease in porosity (50% to 10%) with increase in soak time from 20 to 100 min (Figure 2a). A similar set of experiments performed in a conventional furnace at 1200°C resulted in a slow decrease (50% to 40%) in porosity values from Figure 2a.

² CM bloomerg model no: 0100153

³ TMOS (Si(OCH₃)₄



Fig. 1. Effect of processing technique and temperature on porosity in 8 mol % yttria-zirconia.



Fig 2. Effect of processing technique and time on porosity in 8YZ: (a) 1200°C and (b) 1300°C.

<u>Aerogel</u>

Different stages of microstructural evolution were observed from 600 to 1100°C in a single mode microwave oven and a conventional furnace. Pore volume (Vp) and surface area (SA) evolution as a function of temperature under conventional heat treatment are shown in Figure 3. The percent differences in Vp and SA between the conventional and the microwave treatments are presented in Figure 4. In this figure, the conventional parameter was used as a standard for comparison. If this parameter is bigger than the microwave parameter, then the bar shown is seen as positive. The main factors that influenced these changes in microstructure were analyzed.



Fig.3. Pore volume and surface area evolution in a conventional oven.



Fig. 4. Percent differences in SA and Vp between conventional and microwave heat treatments.

CONCLUSIONS

It can be concluded that the porosities obtained for a microwave-processed zirconia were different that those achieved in a conventional process. It was also observed that, at lower temperature (1200°C), microwave processed samples showed a more significant effect on porosity with respect to soak time than the conventional process.

The data presented on silica aerogel shows that there was a substantial difference between SA and PV in samples processed in conventional and microwave heating between 600 to 1100°C. Moreover, the differences tended to increase in the temperature ranges between 600 and 850°C and 1000 and 1100°C. These differences corroborate a microwave influence on the material studied.

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Effect of Impurities on Microwave Absorption Characteristic of Alumina Sintered Body

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The effect of impurities on microwave absorption characteristic of an alumina sintered body was investigated. High-purity alumina was used as a starting material and the used impurities were sodium, magnesium, iron, or titanium. The samples for measurement of microwave absorption characteristic were sintered beforehand by electric furnace at 1600 °C for 2h. Microwave irradiated to the samples put in a thermal insulation box fabricated by alumina fiber board. In these results, the sample with sodium achieved up to 400 °C for only 5 min. On the other hand, the samples with other impurities were spent for 100 min to achieve up to 400 °C. The sample with sodium indicated higher microwave absorption characteristic than those with other impurities. The presence of β -alumina (Na₂O-11Al₂O₃) was confirmed by powder X-ray diffraction of the sample with sodium. It is considered that the presence of β -alumina in alumina showed high microwave absorption characteristic.

KEYWORDS: α-alumina, impurity, slip casting, microwave absorption characteristic, β-alumina,

INTRODUCTION

Microwave heating take advantage of internal heating, rapid heating and preferential heating over conventional heating process. Microwave heating technique has attracted attention over the years.

The microwave sintering of alumina in various conditions has been reported by many researchers¹⁾⁻⁵⁾. Katz and Blake¹⁾ achieved 99% dense alumina. The total processing time by microwave heating was over 100 min and the final sintering temperature was over 1400°C. The final grain sizes were in the range of 5-50 μ m. J. Cheng *et al.* reported that transparent alumina samples have been successfully prepared by microwave sintering processing²⁾. In comparison to the conventional sintering processing, microwave sintering to transparent alumina can be achieved at lower sintering temperature and shorter sintering time.

We have already reported that an alumina body could be sintered rapidly by microwave heating^{6),7)}. We developed an idea "isothermal barrier" to inhibit heat transfer through the surface of sample. The isothermal barrier was effective to create the uniform temperature distribution in the ceramics products.

When the kind of the alumina raw material was changed, the heat generation behavior was different occasionally. Therefore, it was considered that impurities contained in the alumina raw material influenced the microwave absorption characteristic. In this study, the effect of impurities

on microwave absorption characteristic of the alumina sintered body was investigated.

EXPERIMENTAL

A commercially available pure α -alumina powder (99.99%, AKP-20, Sumitomo Chem. Co., Ltd., Japan) was used as a starting material. Impurities of sodium, magnesium, iron, and titanium were used for sodium carbonate (Na₂CO₃, Wako Pure Chem. Ind., Ltd., Japan), magnesium oxide (MgO, Kojundo Chem. Lab. Co., Ltd., Japan), iron oxide (Fe₂O₃, hematite, Kojundo Chem. Lab. Co., Ltd., Japan), and titanium oxide (TiO₂, rutile, Kojundo Chem. Lab. Co., Ltd., Japan), respectively.

Samples for microwave heating were fabricated by slip casting method. The alumina powder was wet-ball milled with 0.6 wt% dispersant (D-305, Chukyo Yushi Co., Ltd, Japan) and 15 wt% deionized water for 24 h, and then 0.5 mass% of each impurities as oxide were added to the slurries and mixed by wet-ball milling for 3h. The prepared alumina slurries with impurities were poured into gypsum molds, and the green bodies were demolded after the slurries were solidified. The samples for measuring microwave absorption characteristic were sintered beforehand by electric furnace at 1600 °C for 2h. Microwave at 6kW were irradiated to the samples put in a fabricated by alumina fiber board, as shown in Fig. 1. The measurement of microwave absorption characteristic was evaluated by irradiated time and temperature of a sample. Microwave heating was performed up to 1250 °C, and the temperature of the sample was measured from 400 °C to 1200 °C with a radiation thermometer. X-ray diffraction analysis was conducted for phase identification of alumina with impurities.

RESULTS and DISCUSSION

The microwave absorption characteristic of samples at low temperature range was evaluated by measuring the time to elevated temperature up to 400 °C. This result is shown in Fig. 2. The sample with sodium achieved up to 400 °C for 5 min. On the other hand, the samples with other impurities



Fig. 1. Microwave oven in a thermal insulation box.



Fig. 2. Time spent to generate heat up to 400 °C in each impurity

were spent for 100 min to achieve up to 400 °C. The sample with sodium indicated higher microwave absorption characteristic at low temperature range than the sample with other impurities.

The microwave heating profile of samples from 400 °C to 1200 °C is shown in Fig. 3. The sample with sodium generated the heat at temperature rise of 100 °C min⁻¹. On the other hand, the samples with other impurities showed at a slow temperature rise. The heat generation of these samples showed the same behavior as pure alumina. Impurities except for sodium had little influence on the microwave absorption characteristic of alumina.

The XRD patterns of samples with impurities were shown in Fig. 4. The peaks of corundum were observed in each sample. Some peaks different from other samples were detected in the sample with sodium. These peaks were identified as β -alumina (Na₂O-11Al₂O₃). It is considered that the presence of β -alumina in alumina indicated high microwave absorption characteristic.

We suggest that the microwave absorption characteristic can be controlled by adjusting the amount of sodium. If the microwave absorption characteristic is controlled, the development of the isothermal barrier that is able to control the heat generation speed is expected. In addition, an alumina sample with a low microwave absorption characteristic will be improved by adding a small amount of sodium, and a decrease in the sintering time of the ceramics can be expected.

CONCLUSION

We investigated the effect of impurities on microwave absorption characteristic of alumina sintered body. The sample with sodium indicated higher microwave absorption characteristic than the sample with other impurities. The presence of β -alumina was confirmed by powder X-ray diffraction of the sample with sodium. It is considered that the presence of β -alumina in alumina indicate high microwave absorption characteristic.



Fig. 3. The microwave heating profile of samples form 400 °C to 1200 °C.



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The effects of microwave heating on the formation of SnO₂ thin films coated by sol-gel method

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ABSTRACT

 $SnO_2:Nb(Nb \text{ concentration : } 0~3.0 \text{ at.\%})$ thin films were coated on quartz glass substrates by sol-gel method. After coating, the films were sintered by microwave heating with and without susceptor. In microwave heating, lower resistivity was obtained as compared with that processed by conventional heating, especially, the lowest resistivity in this research was achieved by microwave direct heating. Remarkable grain growth was observed as compared with conventional heating case. It was possible to reduce the resistivity of $SnO_2:Nb$ thin films by sol-gel method and microwave processing in sintering process.

INTRODUCTION

Optically transparent oxides tend to be insulator due to their wide energy band gap. However, transparent conducting oxide (TCO) have both high optical transparency in the visible region and high electrical conductivity. TCOs are applied to optoelectronic devices such as transparent electrodes for flat panel displays^{1,2)} or touch panels³⁾. SnO₂, in a representative of TCOs, is used in applications as front electrodes of solar cells and energy efficient windows^{4,5)} on account of their cost effectiveness and chemical and environmental stability.

Non-doped SnO_2 usually exhibits low electrical conductivity because of its low carrier concentration. It has been reported that SnO_2 exhibits high conductivity by doping with Sb^{5+} (antimony doped tin oxide:ATO)^{6,7)}. However, it is undesirable to use antimony in industrial applications because of its toxicity. We have selected niobium as dopant^{3,8)} to SnO_2 in place of antimony. It has a similar atomic radius to tin and is easy to take penta-valent state. It is expected that Nb acts as a donor in SnO_2 .

TCO films are deposited by physical vapor deposition (PVD) in many cases. TCO films deposited by PVD possess high conductivity. In industrial process, sputtering is adopted because it is easy to obtain high conductivity and to deposit uniformly. But necessity of highly vacuum techniques and low utilization efficiency of sputtering targets become problems to deposit thin films by PVD.

In recent years, sol-gel method is focused because it is easy to coat the films. But TCO films coated by sol-gel method have low conductivity⁹ as compared with those deposited by PVD. It is possible to improve conductivities by controlling sintering atmosphere strictly¹⁰. However, it is demanded to achieve high conductivity by a simple process.

In microwave heating, substances are directly heated *via* microwave-substance interaction. Therefore microwave heating supplies non-equilibrium reaction field having unique features such as rapidly heating, selective heating and high thermal efficiency. It is considered that thermal non-equilibrium reaction leads to generate lattice defects which become source of free carriers in semiconductors. By applying microwave processing for sintering, it is expected to improve the conductivities of TCO thin films coated by sol-gel method.

In this study, SnO_2 thin films with various Nb concentrations were coated by sol-gel method and sintered by microwave heating. Electrical and optical properties of the films were measured in order to investigate the effects of microwave heating for TCO thin films coated by sol-gel method.

EXPERIMENTS

SnO₂ sol and Nb₂O₅ sol (Taki chemical co., ltd. Japan) were used as starting materials and mixed them in Nb concentration of $0\sim3.0$ at.% ($0\leq$ Nb/(Nb+Sn) \leq 0.03). SnO₂:Nb thin films were coated on quartz substrates (10x10x1t) by spin coating using these mixture sol. For sintering by microwave heating, we adopted susceptor heating and direct irradiation. In microwave heating experiments, heating rate, temperature, and keeping time were fixed by PID control. Samples were thickened to repeat coating and sintering one after another. Microwave heating equipment (SMW-099, Instrumentation co., ltd. Japan), which allows the electromagnetic field to be focused by turning three-stub turners, was used. For characterization, FE-SEM (JEOL JSM 7000F) and van der Pauw method (Biolad HAL5500PC), UV-vis(JASCO V-570) are used. Film thickness was measured by FE-SEM observation of the cross section.

RESULTS AND DISCUSSION

Fig.1 shows electrical resistivity of SnO₂:Nb thin films sintered by conventional heating or microwave heating as а function of Nb concentration. In the case of microwave heating, lower resistivities were obtained as compared with conventional heating. Resistivities of these films show dependence on Nb concentration, showing a minimum at 1.0 at. %. Carrier concentration is expected to increase by increasing Nb concentration. However, it is possible to have a minimum resistivity by scattering of the career that originates in ionic impurities or segregation of Nb.

As-coated and pre-heated samples by electric furnace could not be heated by microwave irradiation without susceptor. However, it was



Fig.1 Resistivity of SnO₂:Nb thin films sintered at 800°C as a function of Nb concentration.

found that pre-heating by susceptor above 300°C enables to heat by microwave direct irradiation without susceptor. It was thought that the cause of heating depends on the improvement of conductivity. Accordingly, we compared microwave direct irradiation, susceptor heating, and conventional heating in term of resistivities and surface structures.



Fig.2 Surface structures of SnO₂:Nb thin films (Nb 0.50 at.%) sintered at 600° C in air.

Fig.2 shows surface structures of SnO₂:Nb thin films. In cases of microwave heating, remarkable grain growth was observed at film surfaces as compared with conventional heating. Especially, grain growth is much enhanced by direct microwave irradiation.

To investigate the cause of these phenomena induce by microwave irradiation on electrical properties and surface forms, we tried to heat the films rapidly by putting them into an electrical furnace heated at 600°C. However grain growth and decrease of resistivity were not observed in

this experiment. These results suggest that the grain growth and the decrease of resistivities were not caused by rapid heating but should be explained by the microwave effects. Johnson¹¹) and Meek¹² proposed that driving force for atomic diffusion would rise by temperature gradient between grain surface and grain inside, when assuming that electric field concentrates on grain surface under microwave electromagnetic field. Rybakov et al¹³, offered the model which the driving force would occur by drift of lattice defects originated in electric field to suppose that the lattice defect is charged particles. It is thought that the grain growth took place by these driving forces under microwave electromagnetic field. The degree of grain growth might be changed by the presence of susceptor because the susceptor shields microwave partly. The improvement of resistivities by microwave irradiation was caused by improvement of mobility originated in grain growth and the increase of carrier concentration by the enhancement of dopant solvation.

Fig.3 shows optical transmittance spectra of SnO₂:Nb thin films sintered by microwave direct irradiation in air and the inserted graph shows absolution coefficient (α^2) vs. photon energy (hv). The absolution coefficient (α) was calculated using the measured transmittance and reflectance spectra and the optical band gap energy can be obtained by extrapolating the linear region of α^{2} ¹⁴⁾.

Transmittance spectra indicate that all the SnO₂:Nb thin film coated in this research has high transparency. Inserted graph clearly shows the blue shift of the optical band gap energy of

SnO₂:Nb thin films with increasing Nb concentration. This shift of optical bad gap energy is known as Burstein-Moss shift. Burstein-Moss shift¹⁵⁾⁻¹⁷⁾ explains that blue shift of optical band gap of degenerate semiconductors is caused by increase of free carrier concentration occupying conductive band.

Fig.4 shows Nb concentration dependence of resistvities of SnO₂:Nb thin films sintered by microwave direct irradiation in O₂, air or N₂ atmosphere. At Nb 1.0 at.%, sintered in air, the lowest resistivity in this research (2.5 \times $10^{-3} \Omega$ cm) was obtained. This value is lower than SnO₂:Nb thin films deposited by sputtering³⁾. By sintering in O_2 , resistivities increased as compared with others. Kikuchi et.,al³) reported that oxgen vacancies act an important role for the carrier generation for SnO₂:Nb thin films and concentration of oxygen vacancies may increase because of large distortion of SnO₂ lattice included by doping of Nb⁵⁺. So SnO₂:Nb thin films sintered in O₂ have lower conductivity because of low carrier concentration induced by the generation of oxygen vacancies. In addition, grain size of SnO₂:Nb thin films sintered in O₂ were smaller than those of sintered in air or N₂. Because diffusion of atoms take place through defects, this tendency supports that there are scanty oxygen vacancies in SnO₂:Nb thin films sintered in O_2 .







Fig.4 Resistvities of SnO₂:Nb thin films sintered by microwave direct irradiation in O₂, air or N₂.