

**EVIDENCE FOR THE MICROWAVE EFFECT
DURING HYBRID SINTERING AND ANNEALING
OF CERAMICS**

by

Jianxin WANG

A Doctoral Thesis

Submitted in partial fulfilment of the requirements

for the award of

Doctor of Philosophy of Loughborough University

March 2005

Supervisor: Prof. Jon Binner

Institute of Polymer Technology and Materials Engineering

Loughborough University

© by Jianxin Wang, 2005

ABSTRACT

Enhanced mass transport during the high temperature processing of ceramics by microwave heating, generally known as the 'microwave effect', has been observed by many researchers and some hypotheses have been proposed to explain it. However it is still a controversial issue, centring on temperature measurement accuracy. The primary goal for the present work was to achieve definitive evidence of the microwave effect via the microwave hybrid processing of ceramics using accurate temperature measurement.

Three temperature measurement techniques, viz. thermocouple, pyrometer and optical fibre thermometer, have been investigated to determine their accuracy during the hybrid microwave heating of ceramic materials. The experimental results, obtained from melting point measurement on vanadium pentoxide and the heating of three other materials with different loss factors and thermal conductivities, showed that the optical fibre thermometer was the best choice. An accuracy of $\pm 2^{\circ}\text{C}$ was obtained, provided the probe had been calibrated and was protected from stray radiation from conventional heating elements.

Direct evidence for the microwave effect was sought from experiments involving the sintering and annealing of ceramics at different microwave power levels but using an identical temperature / time profile in each case. Sample temperature was monitored using optical fibre thermometry and sample size, composition and precursor powder size were all varied. Specifically, four main ceramics with different loss factors were investigated, viz. zinc oxide (very lossy), yttria stabilised zirconia (intermediate loss) and alumina and silica (low loss).

The results from the experiments showed that an increase in final density was observed for the samples that saw the highest microwave power level compared to

those sintered using pure conventional heating, nearly 25% in the largest case for zinc oxide with the highest loss factor among the four investigated materials. This was equivalent to an effective temperature increase of approximately 100°C. For the low loss alumina samples, the increase was extremely small, with the yttria stabilised zirconia intermediate between the two. In addition, during annealing of fully dense ZnO ceramic pellets, enhanced grain growth was observed during hybrid heating compared to pure conventional heating. Temperature gradients within the samples, a major potential cause of the effect, were assessed using two different approaches and found to be <10°C, far too small to explain the results. Hence it is believed that definitive evidence for the 'microwave effect' has been found during the microwave processing of ceramics.

Key words: Ceramic processing, the microwave effect, hybrid heating, sintering, annealing, grain growth, zinc oxide, yttria stabilised zirconia, alumina.

ACKNOWLEDGEMENTS

Firstly, I owe a great deal of gratitude to my supervisor, Professor Jon Binner, who has brought me extraordinary research opportunities and constantly forced me to remain focused on achieving my goal. His advice, encouragement and comments helped me to establish the overall direction of the research and to move forward with investigation in depth.

Additionally, I would like to express my sincere thanks to Dr B.Vaidhyanathan for the kind and generous support. I would like to thank my research director, Dr Leno Mascia for giving valuable suggestions. I would also like to extend my thanks to all the staff and people who have helped me.

Finally, I would particularly like to thank the Engineering and Physical Sciences Research Council (EPSRC) for the financial support.

Jianxin Wang
March 2005

This thesis is dedicated to my wife and son, who have been a continuous source of encouragement, support and love.

TABLE OF NOTATION

Symbols

A_{gb}	Cross-sectional area over which diffusion occurs, m^2
a	Radius of spherical particles
B	Magnetic flux density, Wb/m^2
c	Speed of light, $2.998 \times 10^8 m/s$
C	Concentration of solute around a particle of radius R
C_0	Concentration over a flat surface
C^*	The concentration that is in equilibrium with particles of radius R^* that neither grow nor shrink
C_p	Specific heat capacity, $J/kg \cdot K$
C_v	Vacancy concentration
∇C_v	Gradient of vacancy concentration
D	Molecular diameter, displacement flux, diffusion coefficient, grain size
D_α	Diffusivity of vacancies of sort α
D_v	Vacancy diffusion coefficient
E	Electric field, vector of the electric field, V/m
E_m	Energy for an atom to overcome the energy barrier to move, eV
E_v	The activation energy that needs to form a vacancy, eV
E_s	Surface free energy
e	Electron charge, $1.6 \times 10^{-19} C$
e_α	Electric charge of vacancies of sort α , C
F_{gb}	Driving force
f	Frequency, Hz
$f(R, t)$	Distribution function
G	Average grain size
H	Magnetic field (A/m), a function that contains the geometrical and material parameters of the powder system

h	Half the interpenetration distance between the spheres
J	Current flow per unit area per unit time, $\text{mol/m}^2 \cdot \text{s}$
J_a	Flux of atoms into the neck, flux density of vacancies of sort α
K	Constant (0.89)
k_B	Boltzman's constant, $1.381 \times 10^{-23} \text{J/atom K}$
K_{eq}	Equilibrium constant for reaction
l_p	Edge length of the tetrakaidecahedron
$\Delta L/L_0$	Shrinkage
M	Molecular weight (g/mol), magnetization
M_{gb}	Grain-boundary mobility
M_s	Weight of the solid in air, g
M_l	Weight of the solid in liquid, g
m and n	numerical exponents that depend on the mechanism of sintering
n	Ions per unit volume of charge
N	Number of particles
N_α	Dimensionless (normalized to the density of sites in the crystalline lattice)
P	Overall net polarization experienced in a dielectric material, the power that is absorbed per unit volume of a material at any instant of time
P_a	Applied pressure, Pa
P_c	Porosity in a unit cell, %
P_e	Electronic polarization, effective pressure
P_i	Ionic polarization
P_m	Molecular (dipole) polarization
P_s	Interfacial (space-charge) polarization
Q	Potential barrier of energy or activation energy
Q_{abs}	Local density of the heat source
R	Gas constant ($8.31467 \text{J/K} \cdot \text{mol}$), diameter of the model sphere
r	Radii of curvature of the neck surface
r_1 and r_2	Principle radii of curvature for a surface
S_A	Surface area of the system of particles

T	Temperature, K
V	Velocity of deformation, i.e. of crystal surface displacement
V_{bias}	Applied bias voltage, V
V_m	Molar volume, m ³ /mol
V_l	Volume of the tetrakaidecahedron
V_p	Total volume of the porosity per unit cell
v_{gb}	Velocity of grain boundary migration,
W	Work that the external pressure, J
X	Neck diameter, radius of the neck
χ_m	Magnetic susceptibility
dx	Width of the grain boundary
z	Valence
$Tan \delta$	Effective loss tangent
$tan \delta_\mu$	Analogous magnetic loss tangent

Greek

α	Geometrical constant that depends on the shape of boundary
α_T	Transfer constant
α_s	Skin depth
β	Pure x-ray diffraction broadening
Γ	Surface energy, J/m ²
γ_{sv}	Surface energy of the solid /vapour interface, J/m ²
δ	Crystal length
ε	Permittivity, C ² /J.m
ε_0	Permittivity of free space, 8.85×10 ⁻¹² C ² /J.m
ε_∞	Dielectric permittivity under high frequency, C ² /J.m
ε'	Dielectric permittivity, C ² /J.m
ε''	Dielectric loss factor
ε_{eff}''	Effective loss factor
ε_r'	Relative dielectric permittivity, C ² /J.m
ε_r''	Effective relative dielectric loss factor
ε_s	Dielectric permittivity static fields, C ² /J.m
ε_r	Relative permittivity, C ² /J.m

η	Viscosity, $\text{N}\cdot\text{s}/\text{m}^2$
η_ρ	Densification viscosity
κ	Thermal conductivity of the materials, $\text{W}/\text{m}\cdot\text{K}$
λ	Wavelength, $\text{\AA}$
λ_0	Free space wavelength, $\text{\AA}$
μ	Permeability of a material ($\text{Wb}/\text{A}\cdot\text{m}$), mobility,
μ_0	Permeability of free space, $4\times\pi\times 10^{-7}\text{Wb}/\text{A}\cdot\text{m}$
μ'	Permeability, $\text{Wb}/(\text{A}\cdot\text{m})$
μ_r	Relative permeability, $\text{Wb}/(\text{A}\cdot\text{m})$
Ω	Volume of an atom or vacancy
P	Density, g/cm^3
ρ	Density of electric charge (C/m^3), specific gravity of the solid (g/cm^3), density of the liquid (g/cm^3)
σ	Conductivity, S/m
σ_{eff}	Total effective conductivity caused by ionic conduction and displacement currents, S/m
τ	Relaxation time
τ_0	Pre-exponential constant in relaxation time equation expressed by the Arrhenius equation
ϕ	The stress intensification factor
ω	Angle frequency, vacancy volume
χ	Susceptibility

Abbreviations

EDAX	Energy dispersive X-ray spectroscopy
EMF	Electromotive force
FEG-SEM	Field emission gun scanning electron microscopy
OFT	Optical fibre thermometry
TD	Relative theoretical density
Th	Thoumocouple
PMF	Ponderomotive force
YSZ	Yttira stabilised zirconia

LIST OF FIGURES

Figure 2.1. The electromagnetic spectrum.

Figure 2.3. Electronic polarization.

Figure 2.2. The propagation of the plane wave.

Figure 2.4. Ionic polarization.

Figure 2.5. Molecular (dipolar) polarization.

Figure 2.6. Interfacial (space-charge) polarization.

Figure 2.7. Frequency response of permittivity (a) and loss factor (b) for a typical dielectric material showing various phenomena.

Figure 2.8. Schematic diagram illustrating a vacancy (effective charge -1) (a) and an interstitial (effective charge +1) (b) in NaCl.

Figure 2.9. Schematic representation of a potential barrier which a lattice atom ($\bullet$) has to overcome to exchange its site with a vacancy ($\square$). (a) Without an external electric field; (b) with an External electric field. D = distance between two adjacent lattice sites; Q = activation energy.

Figure 2.10. Temperature dependence of $\tan \delta$ for a range of ceramics

Figure 2.11. Thermal runaway in materials under microwave irradiation.

Figure 2.12. Schematic diagram illustrating the interaction of microwaves with materials.

Figure 2.13. Schematic diagram of temperature profiles during conventional and microwave heating.

Figure 2.14. The curvature at any point on a curved surface is given in terms of the two principal radii.

Figure 2.15. Point defects in an elemental solid.

Figure 2.16. Schematic diagram for the formation of a Schottky defect.

Figure 2.17. Schematic diagram for the formation of a Frenkel defect.

Figure 2.18. Densification process for three sintering stages. (a) Initial stage of sintering; model structure represented by spheres in tangential contact. (b) Near the end of the initial stage. Spheres have begun to coalesce. The neck growth

illustrated is for centre- to – centre shrinkage of 4% (c) Intermediate stage; dark grains have adopted the shape of a tetrakaidecahedron, enclosing white pore channels at the grain edges. (d) Final stage; pores are tetrahedral inclusion at the corners where four tetrakaidecahedra meet.

Figure 2.19. The two-sphere mode. (a) the non-densification mechanism and (b) the densification mechanism.

Figure 2.20. The model of grain boundaries for the intermediate stage [71].

Figure 2.21. The movement of an atom from one side of the grain boundary to the other involves a change of Gibbs free energy. When an atom moves from position A to position B, the free energy will decrease, so it is a possible direction for an atom on the boundary to move and the boundary will move in the opposite direction.

Figure 2.22. The mode of the movement of grain boundaries [74].

Figure 2.23. Normal grain growth (a) and abnormal grain growth (b).

Figure 2.24. The change of grain size in grain growth. (a), (b) and (c) show the sequence by which grains B lose sides, whereas grains A gain them. (d) and (e) show the disappearance of grain B, together with sides from grains A.

Figure 2.25. Microwave and conventional sintering densities as a function of temperature.

Figure 3.1. The applicator of the hybrid microwave furnace

Figure 3.2. Melting point measurement

Figure 3.3. The sample being measured by a thermocouple.

Figure 3.4. Sintering curve.

Figure 3.5a. An imaging camera during measurement.

Figure 3.5b. Schematic of an imaging camera during measurement.

Figure 3.6. The dilatometer and the applicator of the hybrid microwave furnace and the schematic of the dilatometer.

Figure 3.7. The flow chart of the ceramographic preparation.

Figure 4.1. The melting point of vanadium oxide measured by the type R thermocouple with 3 mm diameter at different microwave power levels.

Figure 4.2. Pure microwave heating curve of zinc oxide.

Figure 4.3. The melted region on the V_2O_5 pellet due to the focusing of the thermocouple during microwave heating.

Figure 4.4. Pure microwave heating curves of zinc oxide, YSZ and alumina with 1 mm gap between sample and thermocouple (1.5RT), showing critical temperature for thermal runaway temperature caused by discharging.

Figure 4.5. Critical temperatures causing thermal runaway for different distances between thermocouple (1.5RT) and sample for different materials.

Figure 4.6. Digital thermal image of a SiC foam during microwave heating.

Figure 4.7. During conventional heating, when an OFT and thermocouple were pressed against the surface of a sample, the OFT was found to record a higher temperature.

Figure 4.8. Schematic diagram of the set-up used for temperature measurement with an OFT.

Figure 4.9. A schematic diagram of reflection of the radiation from the elements by the V_2O_5 .

Figure 4.10. A schematic diagram of the set-up used for temperature measurement with a shielded OFT. The use of an alumina tube with a coating reduced the effect of radiation from the heating elements.

Figure 4.11. The effect of thickness of a coating on temperature measurement accuracy. During the experiments, the OFT was controlled by a PID system and followed a programme set up. A temperature difference was indicated by a thermocouple (Th) arranged as shown in figure 4.7.

Figure 4.12. FEG-SEM micrographs of zinc oxide, YSZ, alumina and silica powder.

Figure 4.13. Densities of submicron ZnO sintered for one hour by pure conventional power as a function of temperature.

Figure 4.14. Sintering curves of submicron ZnO at (a) 680°C and (b) 780°C using hybrid heating with different microwave power (0, 200 W, 400 W, 600 W, 800 W and 1000 W) – all the curves are identical (central temperature control).

Figure 4.15. Sintering curves of ZnO at (a) 780°C and (b) 900°C using hybrid heating with different microwave power (0, 200 W, 400 W, 600 W, 800 W and 1000 W) – all the curves are identical (surface temperature control).

Figure 4.16. Sintering curves of YSZ at (a) 1100°C and (b) 1200°C using hybrid heating with different microwave power (0, 600 W and 1000 W) – all the curves are identical (surface temperature control).

Figure 4.17. Conventional power control during sintering of ZnO at 680°C during hybrid heating with different microwave power (0, 200 W, 400 W, 600 W, 800 W and 1000 W) (central temperature control).

Figure 4.18. Input of power in 1 hour at sintering temperature (680°C) for different hybrid sintering with different microwave power (0, 200 W, 400 W, 600

W, 800 W and 1000 W) of submicron ZnO.

Figure 4.19. Power control during sintering of YSZ at 1100°C using hybrid heating with different microwave power (0, 600 W, and 1000 W) (surface temperature control).

Figure 4.20a. Density curves of micron ZnO hybrid sintered at 780°C and 900°C (surface temperature control).

Figure 4.20b. Density curves of submicron ZnO hybrid sintered at 680°C and 780°C (surface temperature control).

Figure 4.21a. Density curves of submicron ZnO pellets with different sizes hybrid sintered at 680°C (central temperature control).

Figure 4.21b. Density curves of submicron ZnO pellets with different sizes hybrid sintered at 680°C (central temperature control).

Figure 4.22. Density curves of submicron ZnO sintered at different temperatures during pure conventional heating and hybrid heating with 1000 W microwave power.

Figure 4.23. FEG-SEM micrographs of fracture surfaces of submicron ZnO sintered at 680°C (surface temperature control) using (a) conventional heating and (b) hybrid heating with 1000 W microwave power.

Figure 4.24. FEG-SEM micrographs of fracture surfaces of submicron ZnO sintered at 680°C (central temperature control) using (a) conventional heating and (b) hybrid heating with 1000 W microwave power

Figure 4.25. FEGSEM micrographs of fracture surfaces of micron ZnO sintered at 780°C using (a) conventional heating and (b) hybrid heating with 1000 W microwave power (surface temperature control).

Figure 4.26. Density curves of submicron YSZ hybrid sintered at 1100°C and 1200°C (surface temperature control).

Figure 4.27. Density curves of nao YSZ sintered at 900°C and 1000°C (Surface temperature control).

Figure 4.28. Density curves of submicron 3-YSZ and 10-YSZ hybrid sintered at (a) 1220°C and (b) 1260°C (central temperature control).

Figure 4.29. FEG-SEM micrographs of submicron 3-YSZ sintered at 1100°C using (a) conventional heating and (b) hybrid heating with 1000 W microwave power (central temperature control).

Figure 4.30. Porosity curves of annealed alumina films at 1160°C and 1200°C.

Figure 4.31. FEG-SEM micrographs of sol gel alumina films after annealing.

Figure 4.32. X-ray diffraction pattern for sol gel alumina before annealing and after annealing.

Figure 4.33a. X-ray diffraction pattern for ZnO ceramics sintered at 680°C.

Figure 4.33b X-ray diffraction pattern of 101 plane used for the calculation of grain size.

Figure 4.34. Grain size and density curves of submicron ZnO samples sintered at 680°C using hybrid heating with different microwave power(0, 200 W, 400W, 600 W, 800 W and 1000 W) (central temperature control). The average grain size values were obtained from use of the Scherrer equation on X-ray diffraction data.

Figure 4.35. Sintering and densification curves of submicron ZnO pellets sintered at 680°C using PC and hybrid heating with 600 W mw power.

Figure 4.36. Temperature-time curves for submicron ZnO pellets measuring Ø13×5 mm, sintered at 680°C for 1 hour using different microwave power levels. The surface and central temperatures were recorded.

Figure 4.37. Sintering curves of ZnO pellets with a size of Φ25mm×5mm sintered at 680°C (central temperature control).

Figure 4.38. FEGSEM micrographs of cross section of a submicron ZnO pellet with a size of $\Phi 13\text{mm} \times 5\text{ mm}$ sintered at 680°C using hybrid heating with 800 W microwave.

Figure 4.39. FEGSEM micrographs of cross section of a (submicron) ZnO pellet with a size of $\Phi 25\text{mm} \times 5\text{mm}$ sintered at 680°C using hybrid heating with 600 W microwave power.

Figure 4.40a. The five observed points in the temperature-time curve.

Figure 4.40b. Thermal images of the top surface of a ZnO pellet sintered at 680°C with pure conventional heating and hybrid heating with 1000 W microwave power.

Figure 4.41. Temperature distributions cross the surfaces of ZnO pellets sintered 680°C in (a) pure conventional heating and (b) hybrid heating with 1000 W microwave power. (The observed points were the same with figure 4.40).

Figure 4.42. Thermal images of top surfaces of 25 mm diameter ZnO pellets sintered at 680°C .

Figure 4.43. Annealing curves of ZnO pellets in pure conventional processing and hybrid processing at 1000°C .

Figure 4.44. FEG-SEM micrographs of submicron ZnO pellets centres before annealing and annealed at 900°C , 1000°C , 1050°C , 1100°C , 1150°C and 1200°C for 5 hours using pure conventional heating and hybrid heating with 1000 W.

Figure 4.45. FEG-SEM micrographs of submicron ZnO pellet centres annealed at 1100°C for 1, 3 and 5 hours in pure conventional heating and hybrid heating with 1000 W microwave power.

Figure 4.46. FEGSEM micrographs of submicron ZnO pellets from three different regions, 1-centre, 2-middle and 3-edge, annealed at 1100°C for 3 hours with pure conventional heating.

Figure 4.47. FEGSEM micrographs of three different regions, 1-centre, 2-middle and 3-edge of submicron ZnO pellets annealed at 1200°C for 5 hours with pure conventional heating.

Figure 4.48. FEG-SEM micrographs of ZnO pellets before annealing after two step sintering.

Figure 4.49. FEGSEM micrographs of nano 3-YSZ pellets after two step sintering.

Figure 4.50. The grain size distribution of submicron ZnO pellets as a function of region before annealing and after annealing at 900°C and 1000°C for 5 hours in pure conventional heating and hybrid heating with 1000 W microwave power.

Figure 4.51. EDAX spectra of ZnO pellets as a function of region before and after annealing.

Figure 4.52. Average grain sizes of annealed ZnO samples as a function of temperature and region (1:centre, 2:middle and 3:edge) during pure conventional (PC) and hybrid heating (HB) with 1000 W microwave power (C + 1000 W Mw) for 5 hours.

Figure 4.53. Average grain size of annealed ZnO samples as a function of time during pure conventional (PC) and hybrid heating (HB) with 1000 W microwave power at 1100°C, 1150°C and 1200°C.

Figure 5.1. A schematic diagram of possible location of a higher temperature profile in large ZnO samples.

Figure 5.2. A schematic diagram of electric field focusing in the neighbourhood of two spherical ceramic particles.

Figure 5.3. Grain growth of ZnO pellets annealed at 1100°C and 1150°C.

ABSTRACT	I
ACKNOWLEDGEMENTS.....	II
TABLE OF NOTATION.....	V
LIST OF FIGURES	IX
Chapter 1. INTRODUCTION	1
Chapter 2. LITERATURE REVIEW	5
2.1. MICROWAVE PROCESSING OF CERAMICS.....	5
2.1.1. MICROWAVE FUNDAMENTALS AND MICROWAVE HEATING	5
2.1.1.1. <i>CHARACTERISTICS OF MICROWAVES</i>	5
2.1.1.2. <i>POLARIZATION MECHANISMS OF MATERIALS</i>	6
2.1.1.2.1. Electronic Polarization.....	7
2.1.1.2.2. Ionic Polarization	7
2.1.1.2.3. Molecular (Dipolar) Polarization	8
2.1.1.2.4. Interfacial (Space-Charge) Polarization.....	9
2.1.1.2.5. Frequency Dependence of the Different Contributions	9
2.1.1.2.6. Ionic Mechanisms of Conduction in Solid Dielectrics	12
2.1.1.3. <i>LOSS MECHANISMS</i>	14
2.1.1.3.1. Conduction Losses.....	14
2.1.1.3.2. Dielectric Losses	17
2.1.1.3.3. Power Absorption Caused by Dielectric Losses	20
2.1.1.3.4. Penetration Depth.....	20
2.1.1.3.5. Magnetic Losses.....	20
2.1.1.4. <i>MICROWAVE HEATING</i>	21
2.1.2. MICROWAVE SINTERING	23
2.1.2.1. <i>SOLID STATE SINTERING OF CERAMICS</i>	23

2.1.2.1.1.1. Driving force for sintering	24
2.1.2.1.1.2. Diffusion in solids.....	26
2.1.2.1.1.3. Density for three sintering stages.....	30
2.1.2.1.2. Grain Growth in Sintering	38
2.1.2.1.2.1. Normal grain growth.....	39
2.1.2.1.2.2. Abnormal Grain growth.....	41
2.1.2.1.2.3. Topological and interfacial tension requirement of grain growth	45
2.1.2.2. <i>ADVANTAGES OF MICROWAVE SINTERING AND CHALLENGES</i>	
<i>THAT MICROWAVE SINTERING FACES AND THE CURRENT AVAILABLE</i>	
<i>TECHNIQUES APPLIED IN MICROWAVE SINTERING.....</i>	47
2.1.2.2.1. Advantages of Microwave Sintering	47
2.1.2.2.2. Challenges Faced by Microwave Sintering	49
2.1.2.2.3. The Current Available Techniques Applied in Microwave Sintering	50
2.2. MICROWAVE EFFECT	52
2.2.1. MICROWAVE EFFECT	52
2.2.2. MICROWAVE ENHANCEMENT	52
2.2.3. THE NATURE OF THE "MICROWAVE EFFECT"	57
2.2.4. THE EXPERIMENTAL WORK THAT HAS BEEN DONE TO EXPLAIN	
THE "MICROWAVE EFFECT"	59
2.3. TEMPERATURE MEASUREMENT	62
2.3.1. TEMPERATURE MEASUREMENT TECHNIQUES USED DURING MICROWAVE	
PROCESSING	62
2.3.2. THE CHALLENGE THAT TEMPERATURE MEASUREMENT IS FACING DURING	
MICROWAVE PROCESSING AND IT'S ALTERNATIVE.....	62
Chapter 3. EXPERIMENTAL.....	64
3.1. EQUIPMENT	64
3.1.1. TEMPERATURE MEASUREMENT DEVICES	64
3.1.1.1. <i>THERMOCOUPLE</i>	64
3.1.1.2. <i>PYROMETRY</i>	65

3.1.1.3. <i>OPTICAL FIBRE THERMOMETRY</i>	65
3.1.1.4. <i>THERMAL IMAGING CAMERA</i>	65
3.1.2. THE EQUIPMENTS OF CERAMIC SINTERING AND CERAMOGRAPHIC PREPARATION.....	66
3.1.3. THE EQUIPMENT FOR ANALYSIS OF CERAMICS.....	67
3.1.3.1. <i>X-RAY DIFFRACTOMETER</i>	67
3.1.3.2. <i>FIELD EMISSION GUN SCANNING ELECTRON MICROSCOPY</i>	67
3.2. EXPERIMENTAL PROCEDURE	68
3.2.1. EVALUATION OF TEMPERATURE MEASUREMENT TECHNIQUES IN MICROWAVE HEATING.....	68
3.2.1.1. <i>MELTING POINT MEASUREMENT OF V_2O_5</i>	68
3.2.1.2. <i>THERMAL RUNAWAY</i>	69
3.2.2. DENSIFICATION STUDIES	70
3.2.2.1. <i>SELECTION OF MATERIALS</i>	70
3.2.2.2. <i>PROCEDURE FOR SINTERING</i>	70
3.2.3. THERMAL GRADIENT MEASUREMENT.....	74
3.2.4. GRAIN GROWTH	75
3.2.5. IN SITU MEASUREMENT OF SINTERING SHRINKAGE USING A DILATOMETER	76
3.2.6. CHARACTERIZATION	77
3.2.6.1. <i>FIELD EMISSION GUN SCANNING ELECTRON MICROSCOPY EXAMINATION</i>	78
3.2.6.2. <i>X-RAY DIFFRACTOMETER EXAMINATION</i>	78
3.2.6.3. <i>DENSITY MEASUREMNT</i>	78
Chapter 4. RESULTS	80
4.1. EVALUATION OF TEMPERATURE MEASUREMENT TECHNIQUES DURING MICROWAVE HEATING	80
4.1.1. MELTING POINT MEASUREMENT OF V_2O_5 IN MICROWAVE HEATING.....	80
4.1.2. THERMAL RUNAWAY	81

4.1.3. PROBLEMS AND IMPROVEMENT OF OFTS FOR TEMPERATURE MEASUREMENT DURING CONVENTIONAL HEATING	84
4.2. SINTERING EXPERIMENTS	89
4.2.1. SINTERING	89
4.2.1.1. <i>FEG-SEM OBSERVATION OF POWDERS</i>	89
4.2.1.2. <i>THE SELECTION OF SINTERING TEMPERATURES</i>	93
4.2.1.3. <i>TEMPERATURE - TIME PROFILE</i>	93
4.2.1.4 <i>DENSIFICATION</i>	99
4.2.1.4.1. Zinc Oxide	99
4.2.1.4.2. YSZ.....	105
4.2.1.4.3. Alumina.....	108
4.2.1.4.4. Silica	112
4.2.1.5. <i>GRAIN GROWTH IN SINTERING</i>	113
4.2.1.6. <i>DENSIFICATION OBSERVATION USING A DILATOMETER</i>	115
4.3. TEMPERATURE GRADIENTS.....	116
4.3.1. THE USE OF TWO OPTICAL FIBRE THERMOMETER PROBES	116
4.3.2. THE EXAMINATION OF MICROSTRUCTURES	120
4.3.3. THERMAL IMAGING	121
4.4. GRAIN GROWTH OF ZINC OXIDE	125
4.4.1. TEMPERATURE - TIME PROFILES	125
4.4.2. MICROSTRUCTURES AND GRAIN SIZE DISTRIBUTION	126
4.4.3. EDAX ANALYSIS.....	144
4.4.4. GRAIN SIZES OF ANNEALED ZINC OXIDE AS A FUNCTION OF TEMPERATURE AND TIME.....	146
4.4.5. TEMPERATURE GRADIENTS DURING ANNEALING.....	147
Chapter 5. DISCUSSION	148
5.1 EVALUATION OF TEMPERATURE MEASUREMENT TECHNIQUES DURING MICROWAVE HEATING	148

5.1.1. MELTING POINT MEASUREMENT OF V_2O_5 IN MICROWAVE HEATING.....	148
5.1.2. THERMAL RUNAWAY	149
5.1.3. PROBLEMS WITH THE USE OF OFTS FOR TEMPERATURE MEASUREMENT DURING CONVENTIONAL HEATING	150
5.2. SINTERING EXPERIMENTS.....	151
5.2.1. SINTERING	151
5.2.2. DENSIFICATION	152
5.2.2.1. <i>DENSIFICATION OF PELLTS</i>	152
5.2.2.1.1. Enhanced Densification and Factors to Affect Densification.....	152
5.2.2.1.2. Microstructure Observation	156
5.2.2.1.3. Grain Growth in Sintering	156
5.2.2.1.4. Observation Using a Dilatometer.....	157
5.2.2.2. <i>ENHANCED MICROWAVE SINTERING: POSSIBLE EXPLANATIONS</i>	157
5.2.2.2.1 Local Temperature Gradients	158
5.2.2.2.2. Change in Activation Energy.....	160
5.2.2.2.3. Ponderomotive Force.....	161
5.2.2.3. <i>DENSIFICATION OF SOL-GEL ALUMINA FILMS</i>	163
5.2.3. TEMPERATURE GRADIENTS.....	166
5.2.3.1. <i>USING TWO OPTICAL FIBRE THERMOMETERS</i>	166
5.2.3.2. <i>THERMAL IMAGING</i>	167
5.3. GRAIN GROWTH DURING ANNEALING OF ZINC OXIDE.....	168
5.3.1. MICROSTRUCTURES AND GRAIN SIZE DISTRIBUTION.....	169
5.3.2. GRAIN GROWTH KINETICS	170
5.3.3. MECHANISM OF ENHANCED GRAIN GROWTH.....	173
Chapter 6. CONCLUSIONS	175
6.1. EVALUATION OF TEMPERATURE MEASUREMENT TECHNIQUES IN MICROWAVE HEATING.....	175

6.2. EVIDENCE FOR THE MICROWAVE EFFECT DURING HYBRID MICROWAVE SINTERING	177
--	-----

6.3. EVIDENCE FOR THE MICROWAVE EFFECT DURING HYBRID MICROWAVE ANNEALING.....	178
---	-----

6.4. TEMPERATURE GRADIENT MEASUREMENT.....	178
--	-----

Chapter 7. FUTURE WORK.....	179
------------------------------------	------------

REFERENCES	181
-------------------------	------------

Chapter 1

INTRODUCTION

Since about 1970, there has been growing interest in the use of microwaves for heating and material processing. Microwave heating is fundamentally different from conventional heating in which electrical resistance furnaces are typically used. In microwave heating, heat is generated internally by interaction of the microwaves with the atoms and molecules of the material. Microwave heating has many potential benefits, such as rapid heating, selective heating and low cost [1, 2], these are attributable to the volumetric nature of microwave energy deposition. In addition to the possibility of faster and more controllable temperature ramp-up, microwaves can heat one region or phase more than others due to either the method by which the microwaves are deposited in the material or differences in the dielectric properties. The latter is important during the processing of new ceramic and composite materials. All the above can be treated as the thermal action of the electromagnetic field on matter.

In recent years, many researchers have reported unexpected effects resulting from the use of microwave radiation as an alternative energy source during the processing of materials such as sintering, joining, annealing, synthesis, etc [3-56]. More and more researchers have found that a variety of chemical reactions could be accelerated by the microwave irradiation of the reactants. Moreover, the microwave processing of ceramics has also been demonstrated to enhance sintering and grain growth. The enhanced mass transport and solid state reaction rates during the processing of a variety of ceramic, glass, polymer, and other organic and inorganic materials, including lower sintering or reaction temperatures, accelerated kinetics for a wide

range of processes in these materials and reduced activation energies, have broadly been called the “microwave effect”. The latter may therefore be categorised as a “nonthermal” phenomenon [57]. It is now generally, though not unanimously, accepted that a “microwave effect” exists. The primary reasons for any remaining uncertainty are:

- i) The inability to vary the energy source without simultaneously affecting a wide range of other variables. For example, whilst microwave heating experiments are performed in a microwave applicator the corresponding experiments are typically carried out in a separate, radiant furnace of totally different specification (e. g. power level).
- ii) Uncertainties associated with temperature measurement. Pyrometry is often used with microwave heating whilst thermocouples are used in the conventional experiments. When a single technique is used, it is usually a shielded thermocouple - although the presence of the metallic shielding is known to distort the local microwave field. Finally, the surface temperature is usually measured. With conventional heating this will be the hottest part of the specimen, whilst with microwave heating it will be the coolest. This makes a direct comparison of results problematic at best.

The precise nature, origins and magnitude of the effect have not been well established. Two independent investigations have sought to overcome the primary inherent difficulty associated with comparing microwave processing with conventional techniques [58, 59]. Both research groups have attempted to utilise hybrid microwave-conventional heating systems to perform their experiments enabling direct comparisons to be achieved. In the USA, Freeman et al [58] have published results of conductivity measurements made on sodium chloride single crystals under microwave and non-microwave conditions. Their results indicated it is the driving force for diffusion that is enhanced by the application of microwaves rather than the vacancy mobility, which they found was not affected. Similar conclusions were drawn by Wroe and Rowley [59] in the UK based on the sintering of yttria stabilised zirconia (YSZ). They found that an enhancement in densification when using microwaves was consistent with a dependence on the electric field experienced by the material. This suggested that the microwave field was inducing an additional (electric) driving force.

Both these experimental results support the ponderomotive theory first suggested Rybakov and Semenov in Russia [60].

It was believed that a more extensive series of experiments was now required. There was a clear need to:

- a) Identify definitively exactly how accurate temperature measurements are within a microwave environment, hence
- b) Demonstrate conclusively that the ‘microwave effect’ is genuine, and
- c) If genuine, determine its physical basis.

These goals were achieved using a specially designed laboratory scale hybrid microwave/conventional furnace capable of heating samples by pure microwave heating, pure radiant heating or any combination of the two (known as hybrid heating). The system was a conventional furnace built within a multimode microwave cavity and was based directly on the patented work of EA Technology Ltd (EATL)[61].

The first experiments had the primary goal of determining the absolute, and hence also comparative, accuracy of the three most common techniques, viz. shielded thermocouple, pyrometer and optical thermometry. This allowed greater confidence to be achieved in subsequent parts of the research programme.

To investigate the microwave effect itself, a range of experiments were performed in which diffusion, densification and grain growth processes were subjected to different levels of microwave power combined with varied conventional heating whilst maintaining the same heating schedule. Variables included the experimental materials investigated (varying levels of microwave absorption) and sample size. Throughout the work the temperature profile within the sample were monitored.

In addition to obtaining information on the densification characteristics of the different ceramic materials under different heating conditions, systematic evaluation of the microstructure of the sintered materials was performed using routine characterisation techniques. The results from these experiments revealed the dependence of the ‘microwave effect’ on variables such as degree of microwave

absorption, electric field intensity, magnitude of the inverse temperature profile, and material's characteristics.

This report contains six main sections, viz. a literature review, experiments, results and discussion, conclusion, and future work. The literature section introduces the physical aspects of sintering, microwave processing of ceramics, including the interaction of microwaves and materials, and the mechanism of microwave heating, and the microwave effect. The experimental section describes the equipment and experimental procedure for temperature measurement accuracy and the hybrid sintering of ZnO, yttria stabilised zirconia (YSZ), Al_2O_3 and SiO_2 ceramics as well as an in-situ investigation using a dilatometer and grain growth observation in ZnO. The results and discussion section presents and discusses the results obtained to date, including temperature measurement accuracy and the characterisation of the processed ceramics, including X-ray diffraction (XRD) and field emission scanning electron microscopy (FES-EM) observations. The final two sections of the report present the conclusions and future work, respectively.

Chapter 2

LITERATURE REVIEW

2.1. MICROWAVE PROCESSING OF CERAMICS

2.1.1. MICROWAVE FUNDAMENTALS AND MICROWAVE HEATING

2.1.1.1. *CHARACTERISTICS OF MICROWAVES*

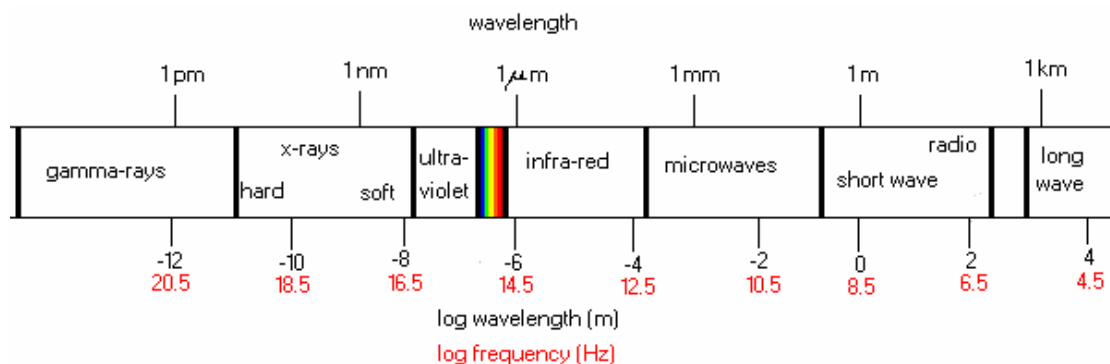


Figure 2.1. The electromagnetic spectrum.

Microwaves cover a broad spectrum of frequencies, usually considered to range from 300 MHz to 300 GHz, figure 2.1. Microwaves travel in the same manner as light waves; they also change direction when travelling from one dielectric material into another; they are reflected by metallic objects, absorbed by some dielectric materials,

and transmitted without significant absorption through other dielectric materials. Microwaves travel in free space at the speed of light, figure 2.2. The free space wavelength λ_0 is related to the frequency by the equation:

$$\lambda_0 = c/f \quad (2.1)$$

Where λ_0 is the free space wavelength, c is the speed of light and f is frequency.

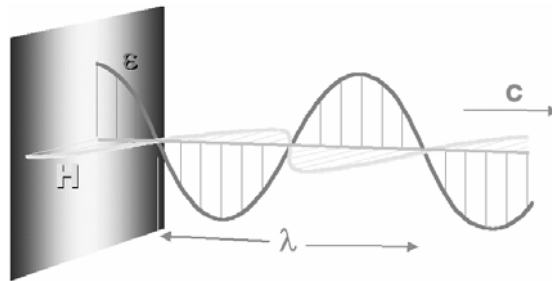


Figure 2.2. The propagation of the plane wave.

2.1.1.2. POLARIZATION MECHANISMS OF MATERIALS

It has long been known that materials may be heated with the use of high frequency electromagnetic waves. The heating effect usually arises from the interaction of the electric field component of the wave with charged particles in the materials. Two major effects, conduction and polarization, are responsible for the heating .

The interaction of microwaves with dielectric materials can cause net polarization in materials. There are several mechanisms which are responsible for this polarization, including: electronic, ionic, molecular (dipolar) and interfacial (space-charge) polarization. Therefore, for a dielectric material the net polarization, P , of the

dielectric material is determined by the sum of the contributions from each mechanism, given by

$$P = P_e + P_i + P_m + P_s \quad (2.2)$$

where P_e is electronic polarization, P_i is ionic polarization, P_m is molecular (dipole) polarization and P_s is interfacial (space-charge) polarization

2.1.1.2.1. Electronic Polarization

This mechanism entails the displacement of the electron cloud relative to its nucleus. It is operative at most frequencies and drops off only at very high frequencies (10^{15} Hz). This mechanism becomes apparent upon application of an electric field (E), under which the electrons are shifted from equilibrium with respect to the positive nuclei in the direction of the field, figure 2.3.

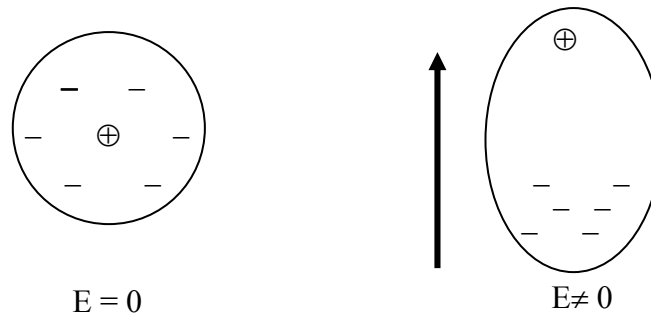


Figure 2.3. Electronic polarization.

2.1.1.2.2. Ionic Polarization

Ionic polarization is defined as the displacement of positive and negative ions toward the negative and positive electrodes, under an applied field (E), the resulting separation of charge yields a displacement of the cations and anions relative to their equilibrium positions, figure 2.4. Ionic resonance occurs in the infrared frequency range (10^{12} to 10^{13} Hz).

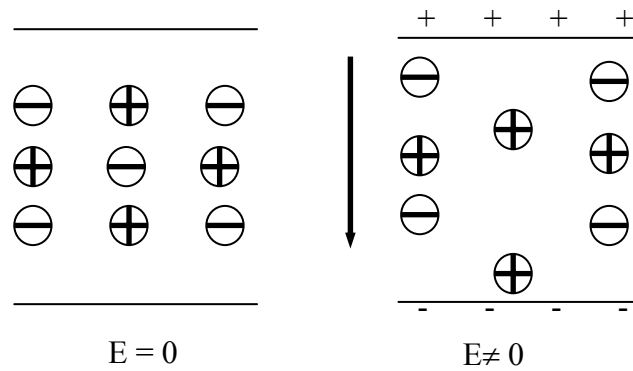


Figure 2.4. Ionic polarization.

2.1.1.2.3. Molecular (Dipolar) Polarization

Molecules are randomly oriented in a material in a normal state so that there is no net charge present. Molecular or dipolar polarization occurs when an external field (E) at low frequencies ($<10^{10}$ Hz) aligns permanent dipoles parallel to the field, figure 2.5. In some materials this polarization can be retained upon removal of the field due to the need for thermal activation of molecular rotation. These electrostrictive or piezoelectric materials are called electrets and are the electric field analogs of magnets.

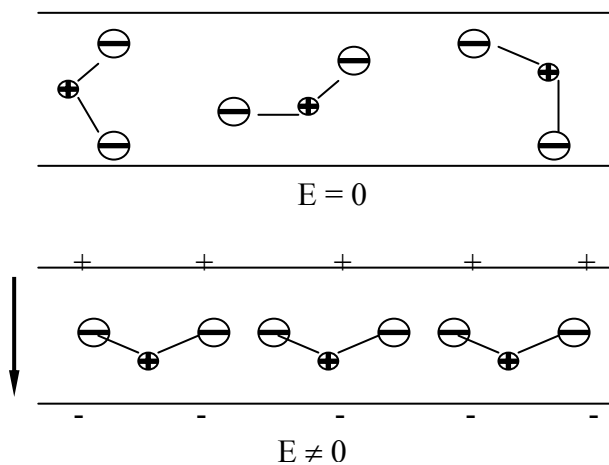


Figure 2.5. Molecular (dipolar) polarization.

Dipolar polarisation is the phenomenon responsible for the majority of microwave heating effects observed in solvent systems. In substances such as water, the different electronegativities of individual atoms results in the existence of a permanent electric dipole on the molecule. The dipole is sensitive to external electric fields and will attempt to align with them by rotation, the energy for this rotation being provided by the field. This realignment is rapid for a free molecule, but in liquids instantaneous alignment is prohibited by the presence of other molecules. A limit is therefore placed on the ability of the dipole to respond to a field, which affects the behaviour of the molecule with respect to frequency, see section 2.1.1.2.5.

2.1.1.2.4. Interfacial (Space-Charge) Polarization

In interfacial or space-charge polarization, mobile charge carriers in a heterogeneous material are accelerated by an applied field until they are impeded by, and pile up at, physical barriers. This build up of charge dictates the polarization of the material. Grain/phase boundaries and free surfaces are common barriers, figure 2.6.

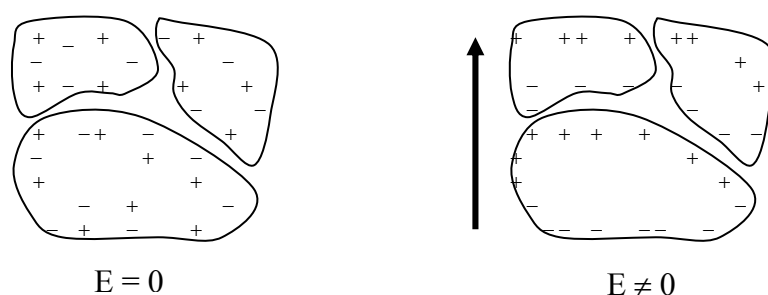


Figure 2.6. Interfacial (space-charge) polarization.

2.1.1.2.5. Frequency Dependence of the Different Contributions

For any material, both the real and complex dielectric permittivities vary with frequency due to the effect of the changing electric field on the movement of the dipoles. Figure 2.7 shows the frequency response of the permittivity and loss factor

for a typical dielectric material showing various phenomena caused by different polarisation mechanisms across the electromagnetic spectrum.

Under low frequency irradiation, the dipole may react by aligning itself in phase with the electric field. Whilst some energy is gained by the molecule by this behaviour, and some is also lost in collisions, the overall heating effect is small. Under the influence of a very high frequency electric field, on the other hand, the dipoles do not have sufficient time to respond to the field, and so do not rotate. As no motion is induced in the molecules, no energy transfer takes place, and therefore, no heating.

Between these two extremes, at frequencies which are approximately those of the response times of the dipoles, is the microwave region. The microwave frequency is low enough that the dipoles have time to respond to the alternating field, and therefore to rotate, but high enough that the rotation does not precisely follow the field. As the dipole re-orientates to align itself with the field, the field is already changing, and a phase difference exists between the orientation of the field and that of the dipole. This phase difference causes energy to be lost from the dipole in random collisions, and gives rise to dielectric heating.

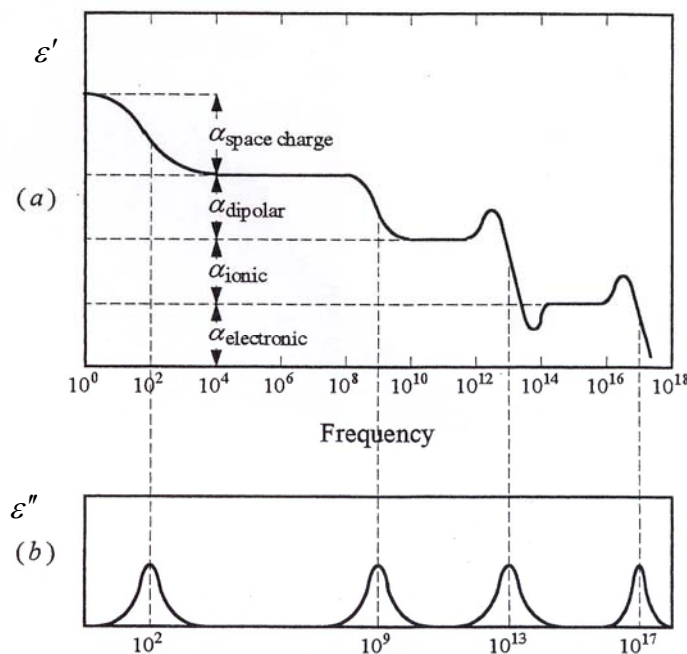


Figure 2.7. Frequency response of permittivity (a) and loss factor (b) for a typical dielectric material showing various phenomena [62].

Debye formed the basis for our current understanding of dielectrics in his theoretical expressions of ε' and ε'' in terms of other material properties [63]. The dielectric permittivity ε' and dielectric loss factor ε'' are dependent on both frequency and temperature, the first of which is expressed explicitly in the Debye equations whilst temperature is introduced indirectly through other variables;

$$\varepsilon' = \varepsilon_{\infty} + \frac{\varepsilon_s - \varepsilon_{\infty}}{\varepsilon + \omega^2 \tau^2} \quad (2.3)$$

and

$$\varepsilon'' = \frac{(\varepsilon_s - \varepsilon_{\infty})\omega\tau}{(1 + \omega^2 \tau^2)} \quad (2.4)$$

where ε_{∞} and ε_s are dielectric permittivities under high frequency and static fields respectively and ω is angular frequency. According to Debye, from Stoke's theorem the relaxation time τ was written

$$\tau = \frac{\pi\eta D^3}{2k_B T} \quad (2.5)$$

where D is the molecular diameter, η the viscosity, k_B Boltzman's constant, and T the temperature. The Debye equations plotted against $\omega\tau$, with arbitrary values for ε_{∞} and ε_s are shown in figure 2.7.

In solids, the molecular dipoles are no longer free to rotate as they are in liquids, but are restricted to a number of equilibrium positions, separated by potential barriers. Theoretical treatments of this behaviour have been formulated and are similar to those developed for liquids. The simplest model for this behaviour assumes that there are two potential wells separated by a potential barrier of energy Q . This represents the two possible orientations of the dipole. Through statistical mechanics, it is found that the relaxation time is related to the potential barrier by;

$$\tau = \tau_0 e^{Q/kT} \quad (2.6)$$

Where τ_0 is a temperature dependent constant. In fact, most dipolar solids exhibit extremely small dielectric losses since Q tends to be extremely large. Water-free ice, for example, does not heat significantly under microwave irradiation.

2.1.1.2.6. Ionic Mechanisms of Conduction in Solid Dielectrics

There are two simple ways in which an ion may pass through the short range ordering of atoms that exists in all solids. Firstly, it may move simply by squeezing through gaps in the structure, i.e. as an ‘interstitial’. Secondly, it may move by virtue of one structural ion being absent, i.e. a ‘vacancy’ moving in the other direction. This is rather analogous to the electron hole, although here, because structural ions can be alternately positive and negative, the vacancy may be effectively negative or positive respectively. By contrast, an electron hole can only be positive. Vacancies and interstitials are illustrated in figure 2.8. In any ionic solid there is an equilibrium concentration of vacancies and interstitials due to constituent ions jumping out place.

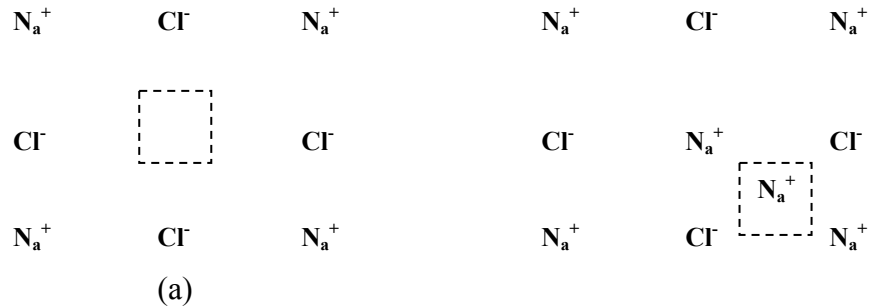


Figure 2.8. Schematic diagram illustrating a vacancy (effective charge -1) (a) and an interstitial (effective charge +1) (b) in NaCl.

Considering one dimension and the x direction only and assuming n ions per unit volume of charge Ze , from the definition of mobility μ , current flow J per unit area per unit time can be described by

$$J = nze\mu E \quad (2.7)$$

and conductivity can be expressed by

$$\sigma = \frac{J}{E} = nze\mu \quad (2.8)$$

where E is the electric field.

When ions move in a crystalline solid, they must have sufficient energy to pass over an energy barrier, figure 2.9. In addition, there must be a vacancy next to a given atom in order for an ion to be able to change its position. Thus, it is clear that n depends on the vacancy concentration in the solid (i.e, on the number of Schottky defects, see 2.1.2.1 1.2.).

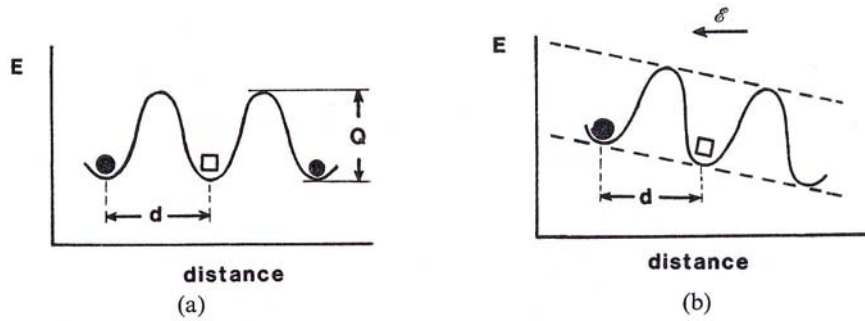


Figure 2.9. Schematic representation of a potential barrier which a lattice atom (●) has to overcome to exchange its site with a vacancy (□). (a) Without an external electric field; (b) with an External electric field. d = distance between two adjacent lattice sites; Q = activation energy.

From Fick's first and second laws [64] (see 2.1.2.1 1.2), the Einstein relation [65] will be obtained:

$$\mu = \frac{De}{K_B T} \quad (2.9)$$

where D is the diffusion coefficient which varies with temperature and relates to special ions. It can be expressed by an Arrhenius equation,

$$D = D_0 \exp \left[- \left(\frac{Q}{k_B T} \right) \right] \quad (2.10)$$

where D_0 is the pre-exponential factor which depends on the vibrational frequency of the atoms and some structure parameters. Q is the activation energy for diffusion of ions in a solid. Then equation 2.8 becomes

$$\sigma = \frac{ne^2 D_o}{k_B T} \exp \left[- \left(\frac{Q}{k_B T} \right) \right] \quad (2.11)$$

Actually, $Q = E_v + E_m$. E_v is the activation energy that needs to form a vacancy and E_m is the energy for an atom to overcome the energy barrier to move. From the equation, it is easy to see that the conductivity of a solid greatly depends on the absolute temperature, the number of defects and ions and their activation energies in this solid. For polycrystalline materials, it appears to be reasonable to assume that the vacant lattice sites provided by the grain boundaries would be used by ions as preferred paths for migration, therefore, the conductivity will be enhanced.

2.1.1.3. LOSS MECHANISMS

There are different mechanisms by which microwaves can couple to a material and a whole host of ways that the microwave energy causes heating in the system. The main loss mechanisms are conduction losses, dielectric losses and magnetic losses. The different mechanisms have different dependencies on properties such as sample type, microstructure, frequency and temperature. Conduction losses dominate in metallic and high conductivity materials such as semiconductors.

2.1.1.3.1. Conduction Losses

Electronic conduction can play a key role in the microwave heating of metal, conductive materials and semiconductors. Such kind of materials can be heated through direct conduction effects resulting from an ohmic type of loss mechanism when the current flows in the material under the action of microwaves. The complex dielectric permittivities may be expressed to take account of these losses by including a separate conduction term as will be seen later.

The importance of conduction losses is displayed by a large number of systems. The addition of dissolved salts in water markedly affects the dielectric properties as conduction increases, and may become important enough to swamp the dielectric losses. On the other hand, the dielectric losses of the majority of solids arise

predominantly from these conduction terms, and may be strongly affected by temperature as has been discussed above. The conductivity of alumina, for example, increases with temperature as electrons are promoted into the conduction band from the O(2p) valence band leading to increases in the permittivity. This is illustrated in figure 2.10 along with a number of other ceramic materials which exhibit similar behaviour [10]. As the temperature increases so too does the dielectric loss factor and heating becomes more effective [66, 67] and dT/dt increases rapidly, as illustrated for strontium titanate and alumina in figure 2.11. Without careful monitoring of these materials under microwave irradiation, their temperature may rise to undesirably high levels.

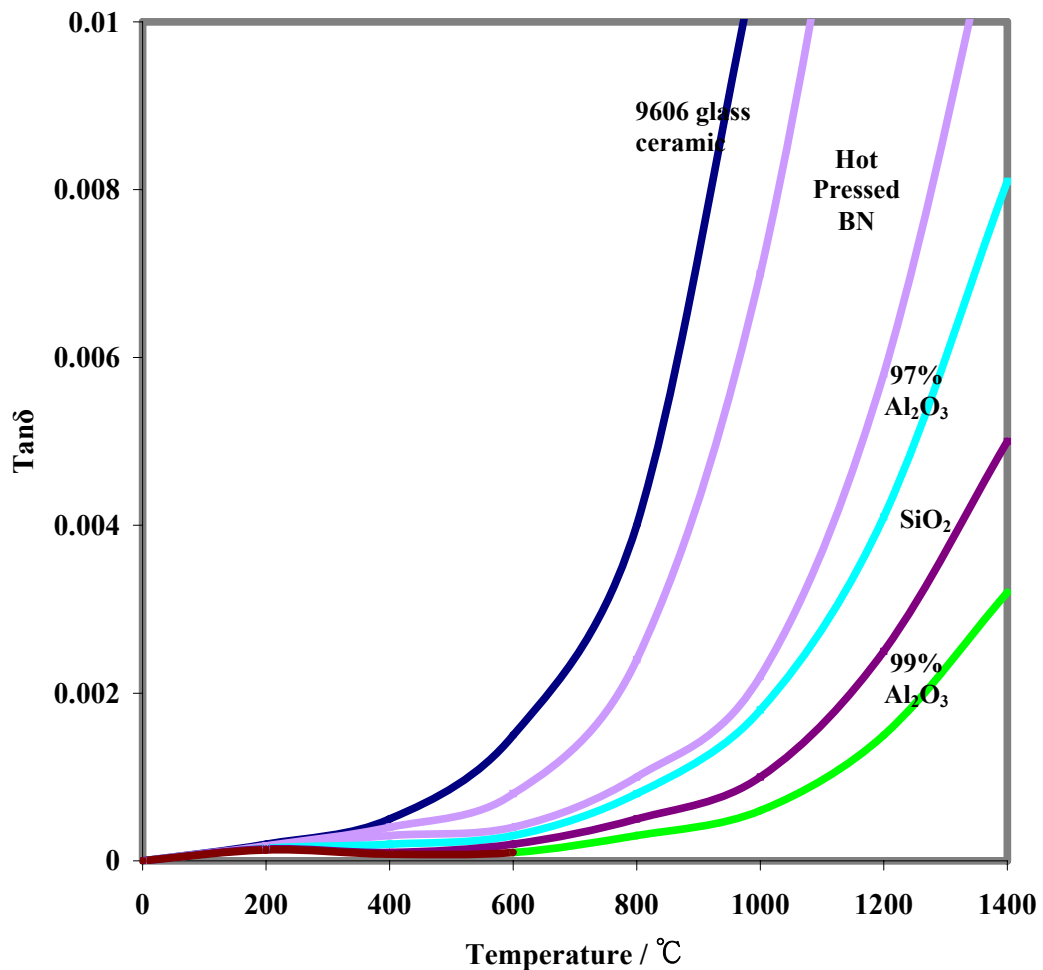


Figure 2.10. Temperature dependence of $\tan \delta$ for a range of ceramics [10].

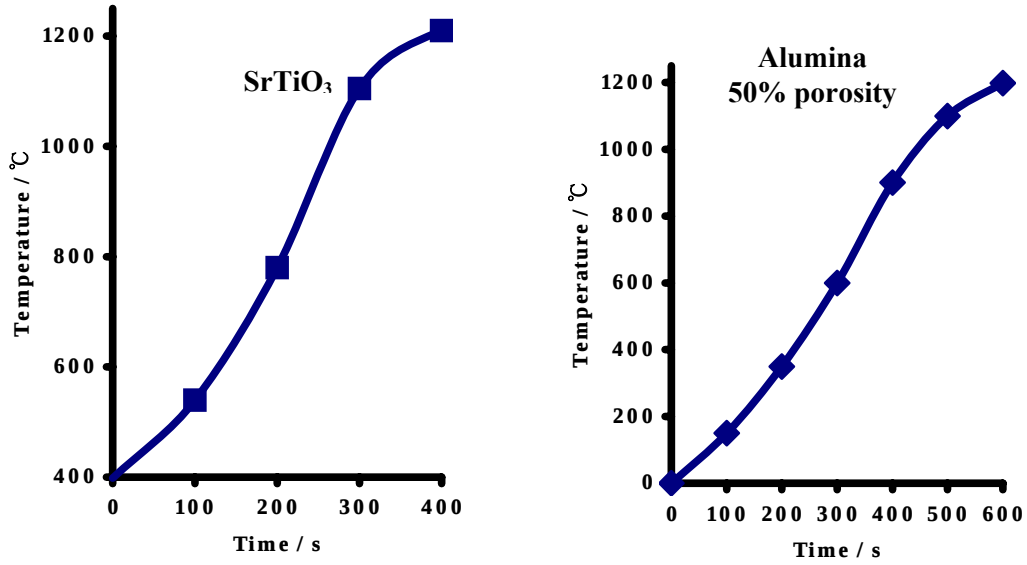


Figure 2.11. Thermal runaway in materials under microwave irradiation [66].

When the conductivity of the material is very large, the fields attenuate rapidly toward the interior of the sample. This is called the skin effect. The latter involves the magnetic properties of the material. When a large current flows in the sample, an interaction between the magnetic field and the current produces a force that pushes the conducting electrons outward into a narrow area adjacent to the boundary. The extent of this skin-area flow is called the skin depth, α_s . Skin depth is defined as the distance into the sample at which the electric-field strength is reduced to $1/e$; the derivation is available in standard text books [68, 69].

$$\alpha_s = \left(\frac{1}{2} \omega \mu_0 \mu' \sigma \right)^{-\frac{1}{2}} \text{ (m)} \quad (2.12)$$

Where ω is the angle frequency, μ_0 is the permeability of free space, μ' is the permeability and σ is the conductivity.

Skin depths range from several microns to a few meters. For example, at 2.45 GHz, brass and graphite have skin depths of 2.6 and 38 μm , respectively whilst cured epoxy and alumina have skin depths of 0.73 and 187 m, respectively. When the skin depth is larger than the dimension of the sample the effect may be neglected. However, if the skin depth is considerably smaller than the sample size, the penetration of microwave energy will be limited, making uniform heating impossible.

2.1.1.3.2. Dielectric Losses

When microwaves penetrate and propagate through a dielectric material, the internal field generated within the affected volume induces translational motion of free or bound charges such as electrons or ions and rotates charge complexes such as dipoles. The inertial, elastic and frictional forces resist these induced motions and cause losses. In dielectric materials, the absorption (degree of interaction) of microwaves is related to the material's complex permittivity.

According to the theories of electromagnetics [68, 69], the overall net polarization experienced in a dielectric material, P , creates a dipole moment which augments the displacement flux, D . Thus, D is defined by [68, 69]

$$\mathbf{D} = \epsilon_0 \mathbf{E} + \mathbf{P} \quad (2.13)$$

Where the net polarization can be written in terms of the susceptibility, χ

$$\mathbf{P} = \epsilon_0 \chi \mathbf{E} \quad (2.14)$$

Thus the relative permittivity can be defined in terms of the susceptibility which is directly related to the polarization mechanism in a material.

$$\mathbf{D} = \epsilon_0 \mathbf{E} + \mathbf{P} = \epsilon_0 (1 + \chi) \mathbf{E} = \epsilon_r \epsilon_0 \mathbf{E} = \epsilon \mathbf{E} \quad (2.15)$$

where $\epsilon_r = \epsilon/\epsilon_0$ is the relative permittivity, ϵ is the permittivity.

In microwave fields, the complex form ϵ^* can be defined by the equations [1]

$$\epsilon = \epsilon' - j \epsilon'' = \epsilon_0 (\epsilon_r' - j \epsilon_r'') \quad (2.16)$$

where ϵ_0 (8.86×10^{-12} F/m) is the permittivity of free space, ϵ' is dielectric permittivity, ϵ'' is dielectric loss factor, the real part ϵ_r' is the relative dielectric permittivity and the

imaginary part ϵ_r'' is the effective relative dielectric loss factor. ϵ' is characterised as a measure of the electrical polarisation of the materials, i.e. the ability of charges and dipoles in the materials to respond to the electric field. ϵ'' acts as the limit to which the movement of charges and dipoles irreversibly extracts energy from the electromagnetic field and dissipates it as heat in the material [68].

According to Maxwell's curl equation from Ampere's law[69],

$$\nabla \times \mathbf{H} = \mathbf{J} + \frac{\partial \mathbf{D}}{\partial t} \quad (2.17)$$

Where $\mathbf{J}$ is a conduction current density while $\frac{\partial \mathbf{D}}{\partial t}$ is a displacement current density.

Putting $\mathbf{J} = \sigma \mathbf{E}$, $\mathbf{E} = E_{max} e^{j\omega t}$, (for a sinusoidal electric field) and $\epsilon = \epsilon' - j \epsilon''$ in Maxwell's curl equation from Ampere's law, yields

$$\nabla \times \mathbf{H} = \sigma \mathbf{E} + j\omega \epsilon^* \mathbf{E} = \sigma \mathbf{E} + j\omega(\epsilon' - j \epsilon'') \mathbf{E} \quad (2.18)$$

Thus,

$$\mathbf{J}_{total} = j\omega \epsilon_0 \left[\epsilon_r' - j \left(\epsilon_r'' + \frac{\sigma}{\omega \epsilon_0} \right) \right] \mathbf{E} \quad (2.19)$$

Since, with most dielectric measuring techniques, it is difficult to separate the losses due to conduction from those due to polarisation, all form of losses can be grouped together, thus defining an effective loss factor ϵ_{eff}'' given by [68]

$$\epsilon_{eff}'' = \epsilon_r'' + \frac{\sigma}{\omega \epsilon_0} = \epsilon_e''(\omega) + \epsilon_i''(\omega) + \epsilon_m''(\omega) + \epsilon_s''(\omega) + \frac{\sigma}{\omega \epsilon_0} \quad (2.20)$$

Where the subscripts e , i , m , and s refer to electronic, ionic, molecular and space-charge respectively. The $\frac{\sigma}{\omega \epsilon_0}$ is the loss parameter for the conductive loss mechanism. According to equation 2.16, the complex dielectric permittivity is given by

$$\epsilon = \epsilon_0 (\epsilon_r' - j \epsilon_{eff}'') \quad (2.21)$$

which includes the loss factors that are relevant to high frequency heating.

The ratio of the effective loss factor to that of the relative dielectric permittivity is called the effective loss tangent $\tan \delta$, namely,

$$\tan \delta = \frac{\varepsilon''_{eff}}{\varepsilon'_{eff}} = \frac{\varepsilon''_r + \frac{\sigma}{\omega \varepsilon_0}}{\varepsilon'_r} = \frac{\sigma_{eff}}{\omega \varepsilon_0 \varepsilon'_r} \quad (2.22)$$

where σ_{eff} is the total effective conductivity (S/m) caused by ionic conduction and displacement currents.

Tan δ can provide a useful indication of the type of interaction that a material will undergo in a microwave field. Ceramics having a loss tangent lower than 0.01 can be considered to be transparent to microwaves. Highly conductive materials such as metals are opaque to microwaves, so they will produce almost total reflection. But the behaviour of most ceramic materials fall between these two extremes, thus they can absorb microwave to a different degree as indicated in figure 2.12

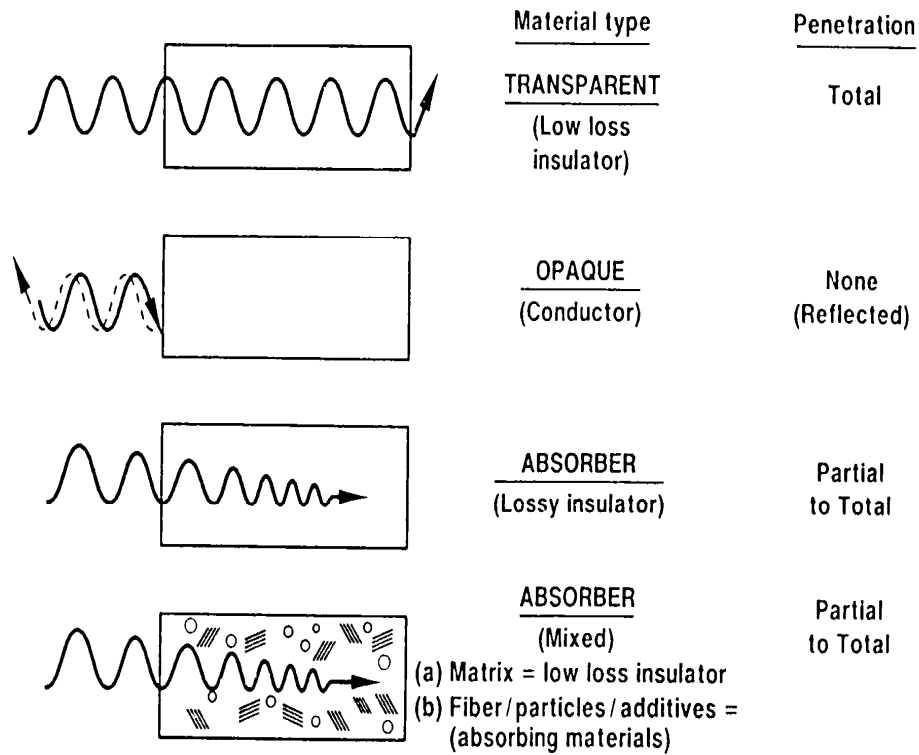


Figure 2.12. Schematic diagram illustrating the interaction of microwaves with materials [10].

2.1.1.3.3. Power Absorption Caused by Dielectric Losses

The power P that is absorbed per unit volume of a material at any instant of time can be described by [68]

$$P = \frac{1}{2} \omega \epsilon_0 \epsilon''_{eff} |E|^2 = \frac{1}{2} \omega \epsilon_0 \epsilon'_r \tan \delta |E|^2 \quad (2.23)$$

where: $|E|$: the magnitude of the electric field and ω is the angle frequency of the electric field.

2.1.1.3.4. Penetration Depth

The depth of penetration, D_p , of the microwaves into the materials is given as [68]:

$$D_p = \frac{1}{2} \omega \left(\frac{\mu_0 \mu' \epsilon_0 \epsilon'}{2} \right)^{\frac{1}{2}} \left\{ \left[1 + \left(\frac{\epsilon''_{eff}}{\epsilon'} \right)^2 \right]^{\frac{1}{2}} - 1 \right\}^{-\frac{1}{2}} \quad (2.24)$$

From the equation, the penetration depth largely depends on the angular frequency of the electric field and the electromagnetic properties of the materials.

2.1.1.3.5. Magnetic Losses

Magnetic polarisation may also contribute to the heating effect observed in materials where magnetic properties exist, and similar expressions for the complex permeability of such materials may be formulated. Although such cases are relatively uncommon, a familiar example of its importance is in the microwave heating of Fe_3O_4 .

In a manner analogous to the case of a dielectric material under the influence of a electric field, a complex permeability is assigned to the following relation [68]:

$$\mathbf{B} = \mu_0 (\mathbf{H} + \mathbf{M}) = \mu_0 (1 + \chi_m) \mathbf{H} = \mu_0 \mu_r \mathbf{H} = \mu \mathbf{H} \quad (2.25)$$

where B is the magnetic flux density, H is the magnetic field, M is the magnetization, μ_0 is the permeability of free space, χ_m is the magnetic susceptibility, μ is the permeability of a material, and μ_r is the relative permeability

In an analogous way to the electric losses, the losses that are due to a time varying magnetic field can be described by a complex relative permeability

$$\mu_r = \mu' - j\mu'' \quad (2.26)$$

Where μ' is the permeability and μ'' describes all magnetic losses.

An analogous magnetic loss tangent, $\tan \delta_\mu$ can also be defined as [68]

$$\tan \delta_\mu = \frac{\mu''}{\mu'} \quad (2.27)$$

Similarly, the power that is absorbed per unit volume of the material at a given instant in time can be described by [68]

$$P = \frac{1}{2} \omega \mu_0 \mu'' |H|^2 = \frac{1}{2} \omega \mu_0 \mu' \tan \delta |H|^2 \quad (2.28)$$

Where ω is the angle frequency, μ_0 is the permeability of free space and μ' is the permeability

2.1.1.4. MICROWAVE HEATING

The thermal phenomenon in a material can be described by the governing equation:

$$C_p \rho \frac{\partial T}{\partial t} = \nabla(\kappa \nabla T) + Q_{abs} \quad (2.29)$$

where C_p is specific heat capacity, ρ is density, κ is thermal conductivity of the materials and Q_{abs} is local density of the heat source. In microwave heating, Q_{abs} is described by the equation 2.23 and related to the depth of penetration, D_p , of the microwaves into the materials given by the equation 2.24, therefore, it is easy to see that the temperature profile or temperature distribution in microwave heating is dependent on many factors such as power level, electric field distribution and the properties of sintered materials including heat losses, thermal and electrical conductivity, *etc.*.

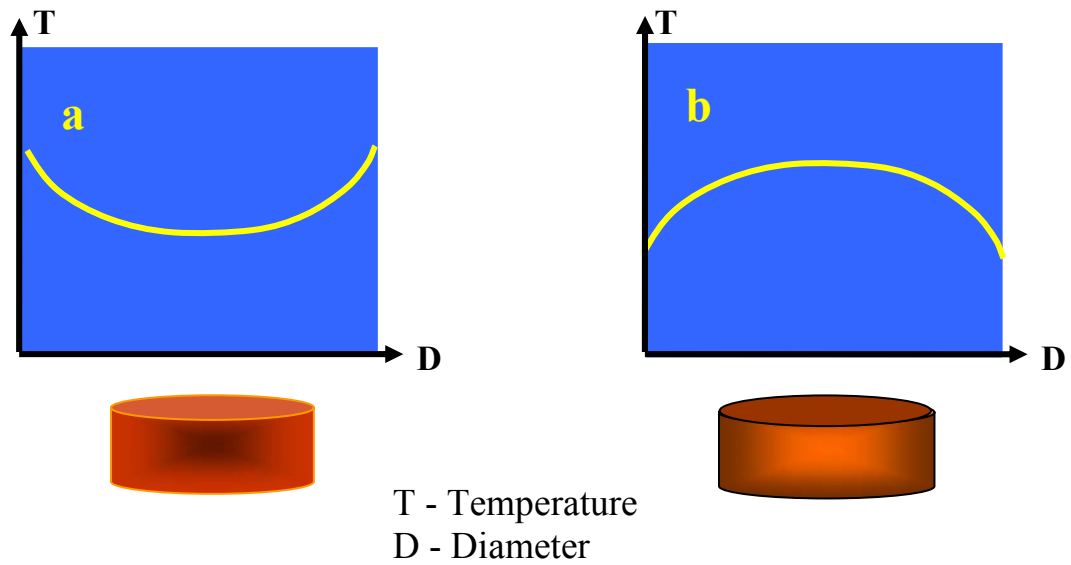


Figure 2.13. Schematic diagram of temperature profiles during (a) conventional and (b) microwave heating.

As shown above, microwaves can create heat by the mechanisms of conduction losses, dielectric losses and magnetic losses. A distinguishing feature of microwave heating is its volumetric nature. This is because microwave power is directly deposited into the ceramic by the interaction between microwaves and materials. Because the surrounding air remains cooler than the body, it can result in the creation of an inverse temperature profile with time, *i.e.* a hotter interior than the surface, while conventional heating relies on thermal conduction and radiation to transport heat from the surface of the ceramic to the centre of the body [10], figure 2.13. Another source of temperature gradients in microwave heating is the inhomogeneous distribution of the microwave power dissipated in the material, which is directly related to the

inhomogeneous absorptivity of the material and the inhomogeneous electric field strength.

2.1.2. MICROWAVE SINTERING

2.1.2.1. SOLID STATE SINTERING OF CERAMICS

2.1.2.1.1. Densification

The densification of a particulate ceramic compact is technically referred to as sintering, which is a process whereby a heat treatment is used to convert a green body into a rigid, polycrystalline solid that is usually dense.

The sintering process plays a prominent role in the fabrication of ceramics. Almost all ceramic bodies must be fired at elevated temperatures to achieve densification and produce microstructures in which the size and shape of the grains, the amount of porosity, the pore size, the distribution of the pores in the structure, and the nature and distribution of any second phases, influence the properties of ceramics. Densification is a natural consequence of sintering - as the particles change shape to increase their contact area with neighbouring particles, the pores that comprised the former interparticle spacing are driven toward free surfaces. The loss of pores during sintering results in a volume reduction and therefore a density increase of the compact. Sintering is accompanied not only by the densification but also by the grain growth of the ceramic.

The following criteria must be met before sintering can occur:

1. A driving force must be present.
2. Material transport must be present .
3. Energies to activate and sustain this materials transport must be present.

A major driving force for this process is the reduction in the total free energy of the system, this arises principally from the elimination of a substantial fraction of the gas/solid interface of the original powder compact. The main mechanisms for

transport are diffusion and viscous flow. Heat is the primary source of energy, in conjunction with energy gradients due to particle-particle contact and surface tension.

2.1.2.1.1.1. Driving force for sintering

As with all other irreversible processes, sintering is accompanied by a lowering of the free energy of the system. The sources which give rise to this are usually referred to as the driving forces for sintering. The possible alternatives are: a) the surface energy, b) an externally applied pressure, c) a chemical reaction as well as others.

A. The surface curvature and sintering stress

Assuming 1 mole of powder consists of spherical particles with a radius a . The number of particles is

$$N = \frac{3M}{4\pi a^3 \rho} = \frac{3V_m}{4\pi a^3} \quad (2.29)$$

where ρ is the density of the particles, which are assumed to contain no internal porosity, M is the molecular weight, and V_m is the molar volume.

The surface area of the system of particles is

$$S_A = 4\pi a^2 N = \frac{3V_m}{a} \quad (2.30)$$

Then the surface free energy associated with the system of particles is

$$E_s = \frac{3\gamma_{sv} V_m}{a} \quad (2.31)$$

where γ_{sv} is the specific surface energy. The surface free energy, E_s , provides a motivation for sintering. If a fully dense body is produced from the 1 mole of material, E_s represents the decrease in surface free energy of the system.

The Laplace equation expresses the stress σ associated with a curved surface as

$$\sigma = \gamma \left(\frac{1}{r_1} + \frac{1}{r_2} \right) \quad (2.32)$$

where γ is the surface energy, and r_1 and r_2 are the principal radii of curvature for this surface. Figure 2.14 depicts a general point on a curved surface and the two radii r_1 and r_2 . When a radius is located inside the mass, the sign convention gives it a positive value (tensile stress): hence, concave surfaces have negative signs (compressive). A flat surface is stress free. During the sintering process, this kind of stress described by the Laplace equation is termed the sintering stress which is associated directly with the curvature at the interparticle neck.

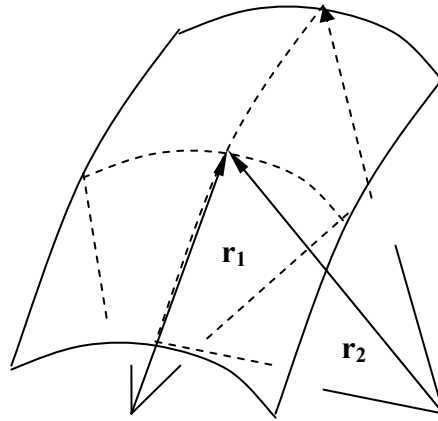


Figure 2.14. *The curvature at any point on a curved surface is given in terms of the two principal radii [70].*

Initially, Mackenzie and Shuttleworth proposed that sintering densification depended on exceeding a critical sintering stress [71]. Densification increases with the sintering stress, which in turn varies with temperature. The sintering stress has been assessed using creep experiments, finite element analysis, photoelastic stress measurements, transmission electron microscopy, and dilatometry. For a typical inorganic material, surface energy is in the range 1 to 2 J/m² and the microstructure scale is often the order of 0.1 to 20 μm . Consequently, the estimated sintering stresses give values in the range 0.05 to 60 MPa, depending largely on the pore size [71]. The highest stresses are measured for small pores and particles. Thus, there is an inherent self-induced stress on particles that acts to generate sinter bonds at high temperatures. With small powders the stress can be significant, leading to a creep process.

B. The pressure

An externally applied pressure can also be a major contribution to the driving force when the pressure is applied over a significant part of the heating process. The work the external pressure does is approximately :

$$W = p_a V_m \quad (2.33)$$

where p_a is the applied pressure and V_m is the molar volume. W represents the driving force for densification provided by the external pressure which is amplified in the microstructure to directly supplement in the sintering stress.

C. Chemical reaction

A chemical reaction may also provide a driving force for sintering. The decrease in free energy accompanying a chemical reaction is given by [71]

$$\Delta G = -RT \ln K_{eq} \quad (2.34)$$

where R is the gas constant (8.3J/mol), T is the absolute temperature and K_{eq} is the equilibrium constant for reaction.

Because the current work on microwave sintering involves just solid-state sintering, there are no pressure or chemical reaction contributions.

2.1.2.1.1.2. Diffusion in solids

Defects

In any crystalline material, there are various defects which control the rate at which matter is transported through the solid state, as well as many other properties. The crystal lattice defects are normally divided into three groups: point defects, dislocations and planar defects. The path of matter transport is determined by these defects.

A point defect is defined as any lattice point which is not occupied by the proper ion or atom needed to preserve the long-range periodicity of the structure and its immediate vicinity. Point defects include missing atoms or vacancies, interstitial atoms occupying the interstices between atoms and substitutional atoms sitting on sites that would normally be occupied by another type of atom.

Point defects consist of two types of defects, namely intrinsic defects and extrinsic defects. Extrinsic defects are created as a result of the presence of impurities in the host crystal while intrinsic defects involve the transfer of atoms from the regular lattice sites as shown in figure 2.15. Two of the more common types of intrinsic defects in ionic crystals are referred to as the Schottky defect, figure 2.16 and the Frenkel defect, figure 2.17. The Schottky defect is caused by the movement of a cation and an anion from their lattice sites to an external surface, leaving behind vacancies. At the surface, the cation and anion form extra perfect crystal. When a cation leaves its regular lattice site and occupies an interstitial site, leaving behind a vacancy; the cation and the vacancy are called a Frenkel defect.

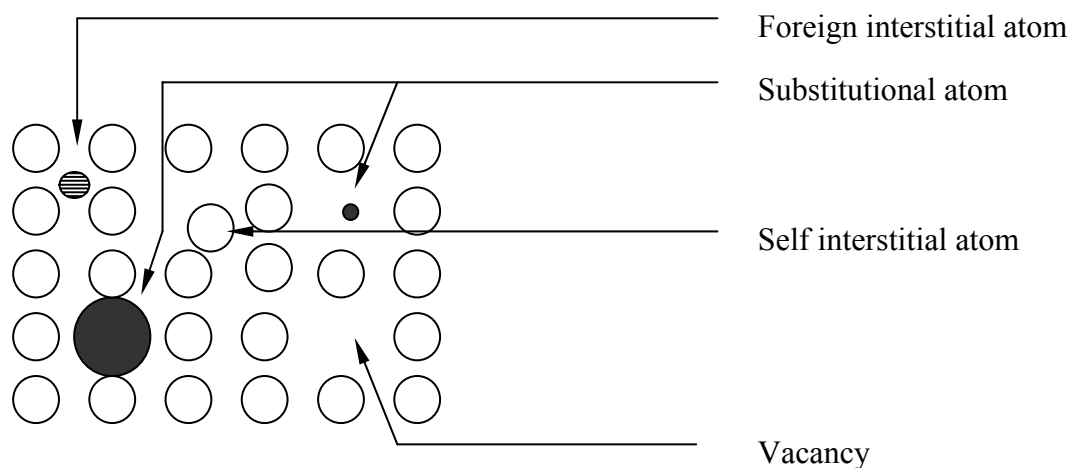


Figure 2.15. Point defects in an elemental solid.

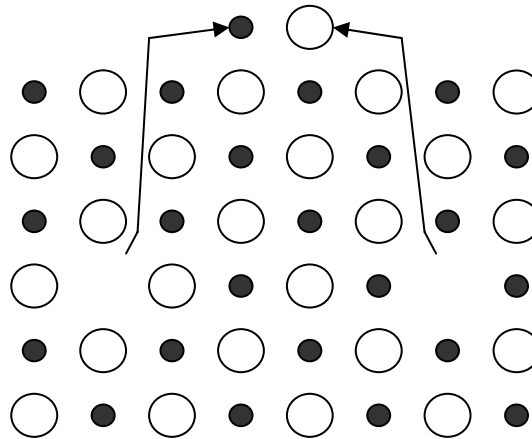


Figure 2.16. Schematic diagram for the formation of a Schottky defect.

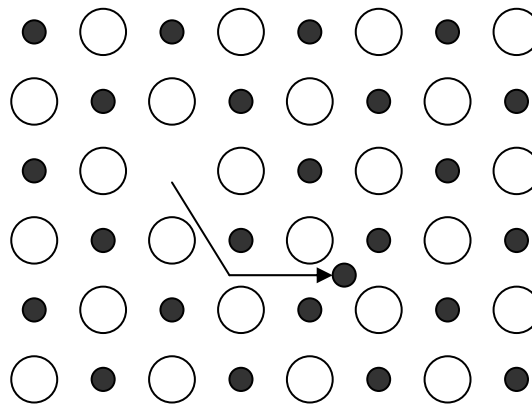


Figure 2.17. Schematic diagram for the formation of a Frenkel defect.

Line defects are characterized by displacements in the periodic structure of the lattice in certain directions, commonly referred to as dislocations, whilst planar defects consist of stacking faults, internal interfaces (e.g., grain boundaries) and free surfaces. The different types of defects determine the path of matter transport. Diffusion along the major paths cause the major mechanisms of matter transport.

Fick's first and second laws

Transport of matter is a vital process in ceramic sintering in which the diffusing species include atoms, ions and molecules. The movement of the diffusing species is driven by gradients in the concentration. The concentration can be considered as a

function of distance and time. The diffusion process can be described by Fick's first and second laws:

$$\mathbf{J} = -D \nabla C \quad (2.35)$$

and

$$\frac{\partial C}{\partial t} = \nabla \cdot D \nabla C \approx D \nabla^2 C = D \left(\frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} + \frac{\partial^2 C}{\partial z^2} \right) \quad (2.36)$$

where $\mathbf{J}$ is the vector with components and represents the number of diffusing species crossing unit area. D is the diffusion coefficient and C is the concentration.

Fick's first law states that the flux of the diffusing species is proportional to the concentration gradient and occurs in the direction of decreasing concentration. The concentration in Fick's first law is independent of time. It displays that concentration gradient is a driving force for diffusion of species. Fick's second law can be derived from his first law and an application of the principle of conservation of matter, but it can describe the change in concentration as a function of time.

Mechanisms of diffusion

The mechanisms of diffusion include lattice diffusion, surface diffusion, grain boundary diffusion, and dislocation pipe diffusion.

Lattice Diffusion

Lattice diffusion, also known as volume diffusion or bulk diffusion, occurs through the movement of point defects. The path of the diffusion is through the bulk of the lattice. The different mechanisms of lattice diffusion are created by the different types of point defects, viz.

- (a) Vacancy mechanism: is a diffusion mechanism in which an atom on a normal lattice site exchanges its position with a vacant site.
- (b) Interstitial mechanism: is a diffusion mechanism in which an atom on an interstitial site moves to one of the neighbouring interstitial sites.

(c) Interstitialcy mechanism: is a diffusion mechanism in which an atom on the regular lattice site exchanges position with a neighbouring interstitial atom.

(d) Direct exchange or ring mechanism: is a diffusion mechanism in which several atoms in a circle exchange their positions simultaneously without the participation of defects.

Grain boundary diffusion

Grain boundary diffusion involves the movement of atoms or vacancies in the boundaries between the crystal grains in polycrystalline materials. Compared to lattice diffusion, the atoms on the grain boundaries have fewer neighbours, so the activation energy for grain boundary diffusion is generally less than that for lattice diffusion. Because of the highly defective nature and the lower activation energy of the grain boundary, grain boundary diffusion is generally more rapid than lattice diffusion. For a relatively constant grain boundary thickness, the fraction which is occupied by the grain boundary in the material increases with decreasing grain size. The rate of grain boundary diffusion is, therefore, dependent on the grain size.

Surface diffusion

Surface diffusion involves the movement of atoms or vacancies in a thin surface layer. Compared to lattice and grain boundary diffusion, the atoms on the surface have fewer neighbours and are less tightly bound, so the activation energy for surface diffusion is less than that for other mechanisms.

2.1.2.1.1.3. Densification for three sintering stages

Sintering is a densification and grain growth process. Densification is a process in which the porosity is removed from the ceramic green body. When the pores change shape without an increase in density, coarsening will take place. Sintering is composed of the three steps, namely, an initial stage, an intermediate stage and an final stage. Table 2.1 and figure 2.18 shows the main parameters and the densification process in the three sintering stages.

Table 2.1. Main parameters in the three sintering stages [71, 72].

Stage	Microstructure feature	Density range	Idealized model
Initial	Particle surface smoothing and rounding of pores, Grain boundaries form, Open pores Neck formation and growth	Up to 0.65	Two monosize spheres contact
Intermediate	Intersection of grain boundaries, Shrinkage of open pores, Equilibrium pore shape with continuous porosity	0.65 – 0.90	Tetrakaidecahedron with cylindrical pores of the same radius along the edges
Final	Closed pores intersect grain boundaries, Equilibrium pore shape with isolated porosity	> 0.90	Tetrakaidecahedron with spherical monosize pores at the corners

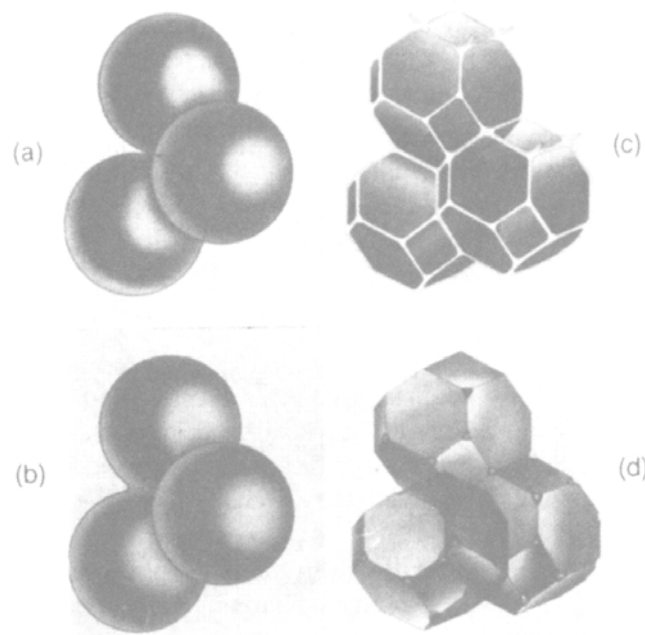


Figure 2.18. Densification process for three sintering stages. (a) Initial stage of sintering; model structure represented by spheres in tangential contact. (b) Near the end of the initial stage. Spheres have begun to coalesce. The neck growth illustrated is for centre- to – centre shrinkage of 4% (c) Intermediate stage; dark grains have adopted the shape of a tetrakaidecahedron, enclosing white pore channels at the grain edges. (d) Final stage; pores are tetrahedral inclusion at the corners where four tetrakaidecahedra meet.[73].

Initial stage

The model for this stage consists of two equal-sized spheres in contact, referred to as the two-sphere model, as shown in figure 2.19.

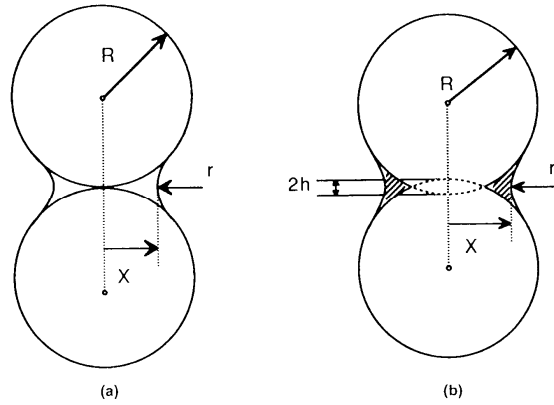


Figure 2.19. The two-sphere mode. (a) the non-densification mechanism and (b) the densification mechanism [71].

The initial stage of sintering is frequently referred to as the neck formation stage, as shown above. The driving force for the initial powder compact comes from the curvature difference between the particle surface and that of the neck. The possible diffusion mechanisms are surface diffusion, lattice diffusion from the surface, lattice diffusion from the grain boundary, vapour transport and viscous flow. The initial stage involves rearrangement of particles and initial neck formation at the contact point between particles. The rearrangement consists of slight movement or rotation of adjacent particles to increase the number of points of contact. Bonding occurs at the points of contact where material transport can occur and where surface energy is highest.

In this stage, a relationship between the neck diameter, X , and time, t , can be expressed in the general form [71]

$$\left(\frac{X}{R}\right)^m = \left(\frac{H}{R^n}\right)t \quad (2.37)$$

where m and n are numerical exponents that depend on the mechanism of sintering and H is a function that contains the geometrical and material parameters of the

powder system. R is the diameter of the model sphere. From this equation, the neck growth depends on the properties and geometrical and material parameters of the powder system.

The shrinkage $\Delta L/L_0$ can also be obtained as a function of time in the general form [71]

$$\frac{\Delta L}{L_0} = -\frac{h}{R} = -\frac{r}{R} = -\frac{X^2}{4R^2} \quad (2.38)$$

where r is the radii of curvature of the neck surface, and h is half the interpenetration distance between the spheres. And [71]

$$\left(\frac{\Delta L}{L_0}\right)^{\frac{m}{2}} = -\left(\frac{H}{2^m R^n}\right)t \quad (2.39)$$

The values of m and n for different diffusions in this initial stage are shown in table 2.2.

Table 2.2. m and n values for the initial stage of sintering [71].

Mechanism	m	n	H
Surface diffusion	7	4	$56D_s\delta_s\gamma_{sv}\Omega/(kT)$
Lattice diffusion from the surface	4	3	$20 D_l\gamma_{sv}\Omega/(kT)$
Lattice diffusion from the grain boundary	5	3	$80 \pi D_l\gamma_{sv}\Omega/(kT)$
Grain boundary diffusion	6	4	$96 D_{gb}\delta_{gb}\gamma_{sv}\Omega/(kT)$
Vapour transport	3	2	$3p_0 \gamma_{sv}\Omega/(2\pi mkT)^{1/2}(kT)$
Viscous flow	2	1	$3 \gamma_{sv}/(2\eta)$

D_s , D_l and D_{gb} are the diffusion coefficients for surface, lattice and grain boundary diffusion; δ_s , and δ_{gb} are the thickness for surface and grain boundary diffusion. γ_{sv} is surface energy; p_0 is the vapour pressure over a flat surface; m is the mass of atom; k is the Boltzmann constant; T is temperature; η is viscosity.

Additionally, taking grain boundary diffusion, the flux of atoms into the neck will be [71]

$$J_a = \left(\frac{D_v}{\Omega}\right)\nabla C_v \quad (2.40)$$

and the volume of matter transported into the neck per unit time will be [71]

$$\frac{dV}{dt} = J_a A_{gb} \Omega, \quad (2.41)$$

where D_v is the vacancy diffusion coefficient, Ω is the volume of an atom or vacancy, ∇C_v is the gradient of the vacancy concentration, A_{gb} is the cross-sectional area over which diffusion occurs, and X is the radius of the neck.

Considering that grain boundary diffusion occurs over a constant thickness δ_{gb} so that $A_{gb} = 2\pi X\delta_{gb}$, and that the vacancy concentration gradient between the neck surface and centre of the neck is assumed to be constant then [71]

$$\nabla C_v = \frac{\Delta C_v}{X} = \frac{C_{v0}\gamma_{sv}\Omega}{XkT}\left(\frac{1}{r_1} + \frac{1}{r_2}\right) \quad (2.42)$$

and it is assumed that $X \gg r$, where r_1 and r_2 are the two principal radii of curvature of the neck surface, and $r_1 = r$ and $r_2 = -X$, and γ_{sv} is the surface energy of the solid /vapour interface. Then the rate of neck growth can be obtained [71]:

$$\frac{1}{X} \frac{dX}{dt} = \frac{16D_{gb}\delta_{gb}\gamma_{sv}\Omega}{kT} \left(\frac{R^2}{X^6}\right) \quad (2.43)$$

From this equation, it is shown that the particle sizes of the powder system and temperature determine the rate of the neck growth.

Intermediate stage

In this stage, more than one mass transport mechanism may be contributing significantly to the changes in microstructure; the densification behaviour is very dependent on the association of pores with grain boundaries and the rate and mode of grain growth.

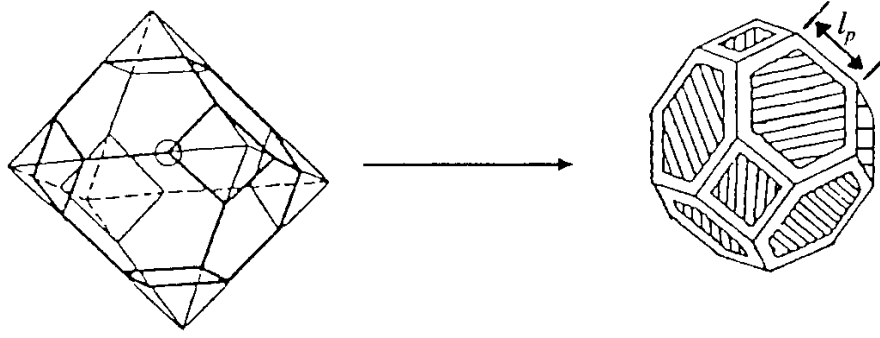


Figure 2.20. *The model of grain boundaries for the intermediate stage [71].*

The geometrical model commonly used for this stage was proposed by Coble [73]. Namely, the powder system is idealized by considering it to consist of a space-filling array of equal-sized tetrakaidecahedra as shown in figure 2.20, each of which represents one particle. The pores are cylindrical and occur along the edges of the tetrakaidecahedron, with the axis of the cylinder coinciding with the edge of the tetrakaidecahedron. The volume of the tetrakaidecahedron is

$$V_l = 8\sqrt{2}l_p^3 \quad (2.44)$$

where l_p is the edge length of the tetrakaidecahedron. If it is assumed r is the radius of the pore, and neglecting the intersections of the pores, then the total volume of the porosity per unit cell is

$$V_p = \frac{1}{3} \times 36 \times \pi r^2 l_p \quad (2.45)$$

The porosity in a unit cell is [71]

$$P_c = \frac{3\pi r^2}{2\sqrt{2}l_p^2} \quad (2.46)$$

For lattice diffusion, assuming: 1) The convergence of the flux to the boundary does not qualitatively change the flux equation with respect to its dependence on the pore radius; 2) The width is equal to the pore diameter; 3) The flux is increased by a factor

of 2 due to the freedom of the vacancy diffusion flux to diverge initially, thereby providing additional available area, then the porosity is given by: [71]

$$P_c \approx \frac{r^2}{l_p^2} \approx \frac{10D_l\gamma_{sv}(t_f - t)}{l_p^3 kT} \quad (2.47)$$

where t_f is the time when the pore vanishes.

The rate of densification is [71]

$$\frac{1}{\rho} \frac{dP_c}{dt} = -\frac{1}{\rho} \frac{d\rho}{dt} \approx \frac{-10D_l\gamma_{sv}\Omega}{\rho l_p^3 kT} = \frac{-10D_l\gamma_{sv}\Omega}{\rho G^3 kT} \quad (2.48)$$

For grain boundary diffusion, using the same model, the porosity and the rate of densification are : [71]

$$P_c \approx \frac{r^2}{l_p^2} \approx \left(\frac{2D_{gb}\delta_{gb}\gamma_{sv}\Omega}{l_p^4 kT} \right)^{\frac{2}{3}} t^{\frac{2}{3}} \quad (2.49)$$

and [71]

$$\frac{1}{\rho} \frac{d\rho}{dt} \approx \frac{4}{3} \times \frac{D_{gb}\delta_{gb}\gamma_{sv}\Omega}{G^4 kT \rho (1 - \rho)^{\frac{1}{2}}} \quad (2.50)$$

From equations 2.48 and 2.50, the densification rate is determined by the diffusion mechanisms, grain size and temperature. The smaller the grain size, the higher the densification rate.

Final stage

In this stage, exaggerated grains separated from pores commonly appear in some regions of the microstructure when the processing is not controlled carefully. The densification behaviour is also very dependent on the final removal of porosity and the rate and model of grain growth. The porosity is removed by vacancy diffusion

along grain boundaries. Therefore, the pores must remain close to the grain boundaries. Pore removal and vacancy diffusion are aided by movement of grain boundaries and controlled grain growth. However, if grain growth is too rapid, the grain boundaries can move faster than the pores and leave them isolated inside a grain. As the grain continues to grow, the pores become further separated from the grain boundaries and have a decreased chance of being eliminated.

For the sintering of polycrystalline materials, the powder system is idealized in terms of an array of equal-sized tetrakaidecahedra with spherical pores of the same size at the corners. A tetrakaidecahedron has 24 pores at corners. The porosity in a tetrakaidecahedron is given by [71]

$$P_s = \frac{8\pi r^3}{8\sqrt{2}l_p^3} = \frac{\pi}{\sqrt{2}} \frac{r^3}{l_p^3} \quad (2.51)$$

For lattice diffusion, a procedure similar to that outlined earlier for the intermediate stage was used by Coble, the porosity is [71, 73]

$$P_s = \frac{6\pi}{\sqrt{2}} \times \frac{D_1 \gamma_{sv} \Omega (t_f - t)}{l_p^3 kT} \quad (2.52)$$

and

$$\frac{1}{\rho} \frac{d\rho}{dt} = \frac{6\pi}{\sqrt{2}} \times \frac{D_1 \gamma_{sv} \Omega}{l_p^3 kT} = \frac{6\pi}{\sqrt{2}} \times \frac{D_1 \gamma_{sv} \Omega}{G^3 kT} \quad (2.53)$$

From this equation, it is indicated that the densification rate also depends on the diffusion mechanisms, grain size and temperature.

The enhanced densification

For the general diffusion mechanisms, the densification rate may be written in the general form:

$$\frac{1}{\rho} \frac{d\rho}{dt} = \frac{3\phi}{\eta_p} (\sum + P_e)$$

where η_p is dimensions of viscosity and can be called the densification viscosity; ϕ is the stress intensification factor and it can be approximated by the expression $\phi = \exp(aP)$, where P is the porosity and a is a parameter that depends on the dihedral angle; $\sum = \frac{\alpha\gamma_{sv}}{r\phi}$ has been called as sintering stress and depends on the microstructural characteristics of the sintering solid; P_e is the effective pressure and depends on the microstructure. Therefore, an enhanced densification may be considered as a direct result of increased sintering stresses, which can appear in different forms. For example, when an external pressure is applied on the sintered samples, it is amplified in the microstructure to directly increase the inherent sintering stress. As a consequence, the effective stress can be several times higher than the applied stress. The applied pressures on the order of 0.1 MPa become significant in enhancing sintering, especially because of stress amplification near pores.

2.1.2.1.2. Grain Growth in Sintering

Grain growth is an integral part of sintering during the final stage because the movement of the grain boundary can be looked upon as that of a broom sweeping out microstructural features such as pores and inclusions. There are two types of grain growth: normal and discontinuous or abnormal, also called secondary recrystallization or canabalistic grain growth. In normal grain growth, the grain size distribution is relatively narrow and has a fixed distribution shape throughout growth. In abnormal grain growth, a few large grains develop and eventually consume all the smaller grains. The grain size and grain distribution control the strength, the creep and the electrical properties and the magnetic properties of the ceramic. Therefore, control of the final grain size is vital.

2.1.2.1.2.1. Normal grain growth

Burke and Turnbull proposed a model for the migration of a grain boundary due to atom transport under a driving force caused by the difference in surface curvature as shown in figures 2.21 and 2.22 [74]. Because of the pressure of the surface curvature, the boundary tends to migrate toward its centre of curvature so that the grain boundary area and its energy can be reduced.

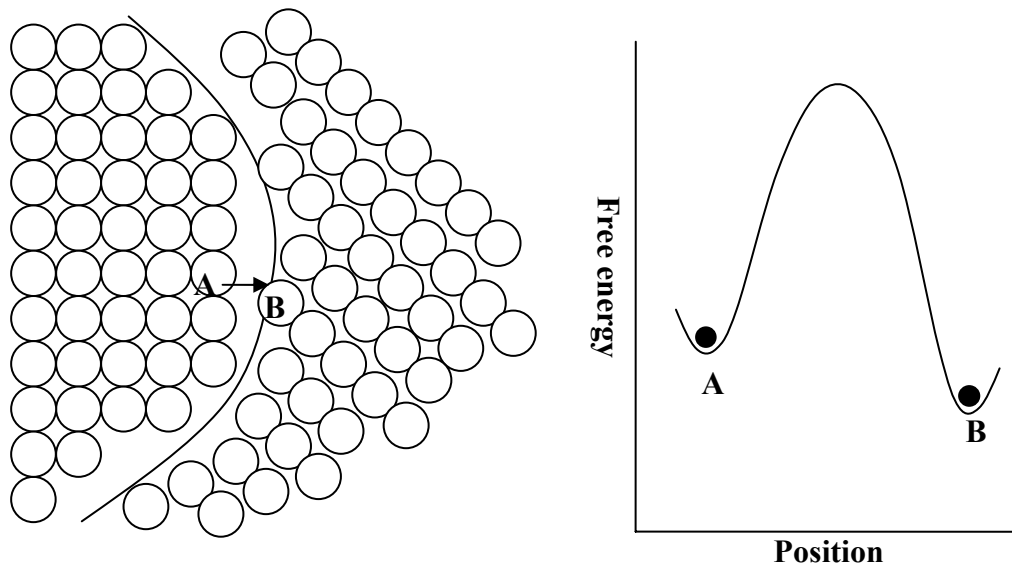


Figure 2.21. The movement of an atom from one side of the grain boundary to the other involves a change of Gibbs free energy. When an atom moves from position A to position B, the free energy will decrease, so it is a possible direction for an atom on the boundary to move and the boundary will move in the opposite direction.

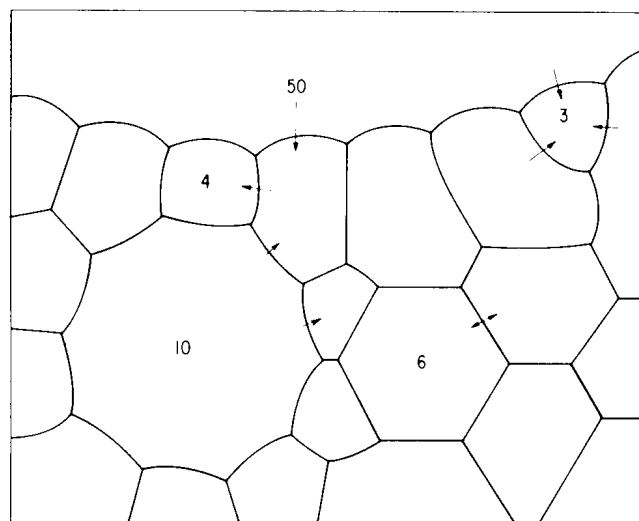


Figure 2.22. The mode of the movement of grain boundaries [74].

A conceptual idea of the change in free energy associated with the diffusion of an atom from one grain to the next is shown in figure 2.22. Due to the pressure of the surface curvature, the boundary tends to migrate toward its centre of the curvature, as this reduces the grain boundary area and hence its energy. For a pure material, the velocity of grain boundary migration, v_{gb} , is given by the product of the grain-boundary mobility, M_{gb} , and the force

$$v_{gb} = M_{gb} F_{gb}, \quad (2.54)$$

where F_{gb} is the driving force

The pressure difference across the boundary is given by the equation of Young and Laplace [71]

$$\Delta p = \gamma_{gb} \left(\frac{1}{r_1} + \frac{1}{r_2} \right), \quad (2.55)$$

where r_1 and r_2 are the principal radii of curvature of the boundary. Assuming that the radii of the boundary is proportional to G , then [71]

$$\left(\frac{1}{r_1} + \frac{1}{r_2} \right) = \frac{\alpha}{G}, \quad (2.56)$$

where α is a geometrical constant that depends on the shape of boundary and G is the average grain size. The driving force for atomic diffusion across the boundary can be taken as the gradient in the chemical potential [71]:

$$F_{gb} = \frac{d\mu}{dx} = \frac{d(\Omega \Delta p)}{dx} = \left(\frac{1}{\delta_{gb}} \right) \left(\frac{\gamma_{gb} \Omega \alpha}{G} \right), \quad (2.57)$$

where Ω is the atomic volume and $dx = \delta_{gb}$ is the width of the grain boundary. The flux of atoms across the boundary is [71]

$$J = \frac{D_{gb}}{\Omega kT} \frac{d\mu}{dx} = \frac{D_{gb}}{\Omega kT} \frac{\gamma_{gb} \Omega \alpha}{\delta_{gb} G} \quad (2.58)$$

where D_{gb} is the diffusion coefficient for atomic motion across the grain boundary. The boundary velocity becomes [71]

$$v_{gb} \approx \frac{dG}{dt} = \Omega J = \frac{D_{gb}}{kT} \left(\frac{\Omega}{\delta_{gb}} \right) \left(\frac{\gamma_{gb} \alpha}{G} \right) \quad (2.59)$$

The driving force is taken as the pressure difference across the boundary, $\gamma_{gb} \alpha / G$, and $v_{gb} \approx \frac{dG}{dt} = M_{gb} F_{gb} = \frac{D_{gb}}{kT} \left(\frac{\Omega}{\delta_{gb}} \right) \left(\frac{\gamma_{gb} \alpha}{G} \right)$, so M_{gb} should be $\frac{D_{gb}}{kT}$. The equation of v_{gb} may be integrated to give [71, 73, 75, 76]

$$G^2 - G_0^2 = \frac{2\alpha M_{gb} \gamma_{gb} \Omega}{\delta_{gb}} t = Kt \quad (2.60)$$

where K is $\frac{2\alpha M_{gb} \gamma_{gb} \Omega}{\delta_{gb}}$.

Experimental measurement of normal grain growth in metals and ceramics has shown that parabolic growth is rarely obeyed. This means that equation 2.60 needs to be improved. For this reason, it is expressed by [71, 73, 75, 76]

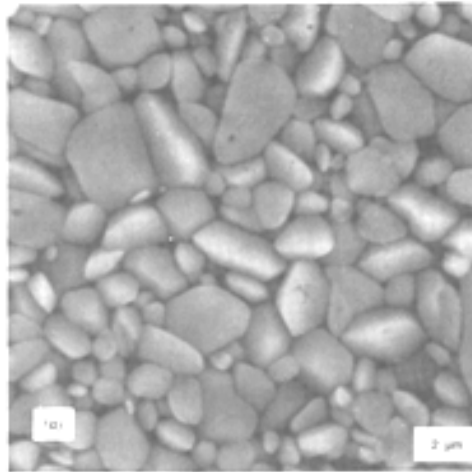
$$G^n - G_0^n = Kt, \quad (2.61)$$

where n is an integer. This equation can also account for impurity drag by various rate determining diffusion steps and pore drag by various rate determining steps [71].

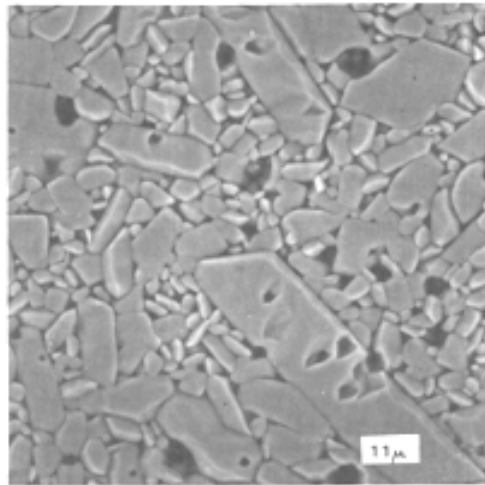
2.1.2.1.2.2. Abnormal Grain growth

Some very large grains can occur in a fine-grained matrix during ceramic sintering. These large grains are referred to as abnormal grains and develop as a result of abnormal or runaway grain growth in which the large grains have a much faster

growth rate than the fine-grained matrix. The faster growth rate is normally explained in terms of the greater driving force for growth of a large grain in a fine-grained matrix relative to that for a small grain in the same matrix. Therefore, the difference in the number of sides between neighbouring grain increase, the curvature of the boundary becomes greater, thereby providing a larger driving force for growth of the large grain, figure 2.23 [71].



a



b

Figure 2.23. Normal grain growth (a) and abnormal grain growth (b) [77].

Supposing R is the critical radius of the grain structure and the other terms are as defined earlier, according to the LSW theory, many features of grain growth and pore growth in sintering can be explained by the Ostwald ripening process [71].

According this theory, a system consists of a dispersion of spherical particles with different radii in a medium in which the particles have some solubility. The chemical potential of the atoms under the surface of a sphere of radius R is given by [71]

$$\mu = \mu_0 + \frac{2\gamma\Omega}{R} \quad (2.62)$$

where μ_0 is the chemical potential of the atoms on a flat surface, γ is the special energy of the interface between the sphere and the medium and Ω is the atomic volume

Because the atoms at the surface of the sphere have a higher chemical potential, they will also have a higher solubility. For ideal solutions, [71]

$$kT \ln\left(\frac{C}{C_0}\right) = \mu - \mu_0 = \frac{2\gamma\Omega}{R} \quad (2.63)$$

where C is the concentration of solute around a particle of radius R , C_0 is the concentration over a flat surface, k is the Boltzmann constant, and T is the temperature of the system. If $\Delta C = C - C_0$ is too small, then $\ln\left(\frac{C}{C_0}\right) = \frac{\Delta C}{C_0}$ and

$kT \ln\left(\frac{C}{C_0}\right) = \mu - \mu_0 = \frac{2\gamma\Omega}{R}$ can be changed into: [71]

$$\frac{\Delta C}{C_0} = \frac{2\gamma\Omega}{kTR} \quad (2.64)$$

From this equation, it is shown that the higher concentration around a particle of smaller radius will lead to a net flux of matter from the smaller particles to the larger ones.

Wagner assumed that the rate of transfer of atoms is proportional to the difference between the solute concentration around a particle of radius R and an average concentration of the solute, C^* , defined as the concentration that is in equilibrium

with particles of radius R^* that neither grow nor shrink. Considering that the change in C^* with increasing R^* can be neglected, the rate of change of the particle radius can be written [78]

$$\frac{dR}{dt} = -\alpha_T \Omega (C_R - C^*) \quad (2.65)$$

where α_T is a transfer constant.

If the total volume of the particles is constant, then [71]

$$4\pi \sum_i R_i^2 \left(\frac{dR_i}{dt} \right) = 0 \quad (2.66)$$

where the summation is taken over all the particles in the system.

Finally putting $R^* = \sum R_i^2 / \sum R_i$, the growth rate of the particle radius can be expressed [71]

$$\frac{dR}{dt} = \frac{2\alpha_T \gamma \Omega^2 C_0}{kT} \left(\frac{1}{R^*} - \frac{1}{R} \right) \quad (2.67)$$

This equation can be expressed [71]

$$\frac{dR}{dt} = 2M_{gb} \gamma_{gb} \left(\frac{1}{R^*} - \frac{1}{R} \right) \quad (2.68)$$

For a distribution function $f(R, t)$, it should satisfy the differential equation [71]

$$\frac{df}{dt} + \frac{\partial(f \frac{dR}{dt})}{\partial R} = 0 \quad (2.69)$$

the distribution function can be expressed by $f(s, t)$. For $0 < s < 2$,

$f(s, t) = [s/(2-s)^5] \exp[-3s/(2-s)]$; for $s > 2$, $f(s, t) = 0$, where $s = R/R^*$. Then the

solution of the equation: $\frac{df}{dt} + \frac{\partial(f \frac{dR}{dt})}{\partial R} = 0$ is [71]

$$(R^*)^2 - (R_0^*)^2 = \left(\frac{2\alpha_T \gamma \Omega^2 C_0}{kT} \right) t = 2M_{gb} \gamma_{gb} t \quad (2.70)$$

Then, [71]

$$\frac{dR^*}{dt} = \frac{M_{gb} \gamma_{gb}}{2R^*} \quad (2.71)$$

The relative growth rate of the large grain can be defined as [27]

$$\frac{d(\frac{R}{R^*})}{dt} = \frac{1}{(R^*)^2} \left(R^* \frac{dR}{dt} - R \frac{dR^*}{dt} \right) = -\frac{M_{gb} \gamma_{gb}}{2RR^*} \left(\frac{R}{R^*} - 2 \right)^2 \quad (2.72)$$

The equation indicates that the relative growth rate of the large grains is always negative except for $R = 2R^*$, in which case it is zero. Abnormal grains therefore do not outstrip the normal grain population but rejoin it at the upper limit of $2R^*$. Furthermore, due to irregularities in their shape and to fluctuations, they can not remain at exactly $2R^*$ after they rejoin the population. They continue to decrease in relative size and are eventually incorporated into the normal distribution.

2.1.2.1.2.3. Topological and interfacial tension requirement of grain growth

Smith considered that for normal grain growth to occur, certain topological requirement of space filling as well as the balance of interfacial tension must be satisfied [79]. Grain boundary energy is a free energy, by definition, so that a polycrystalline body is in a state of excess energy relative to a single crystal and will try to rid itself of grain boundaries as far as it can. As grain boundaries automatically adjust themselves so as to divide space in the most economical manner (i.e. to obtain the lowest surface energy), an overall decrease of the amount of grain boundary can only occur by a decrease in the number of grains. This is achieved by the growth of some grains at the expense of the average grain, i.e. some grains shrink whilst others grow. Just as a pressure difference occurs across the curved surface of a pore leading to atomic diffusion, so diffusion also occurs across a curved grain boundary for the same

reason. The net result is for the boundary to be moved towards its centre of curvature. From an atomistic point of view, an atom on a curved boundary is likely to transfer its allegiance to the concave-faced grain which surrounds it by slightly more than 50%, from the convex-faced grain which surrounds it by slightly less than 50%. A grain with convex faces will thus tend to shrink, and a grain with concave faces will tend to grow. Euler discovered a relation between the numbers of faces F , edges E , and vertices V of a simple polyhedron, as follows:

$$F - E + V = 2 \quad (2.73)$$

In two dimensions, with equilibrium angles of 120° between grain boundaries, it is easy to see that grains with five or less sides will be convex and will shrink whilst grains with seven or more sides will be concave and grow. Grains with the average number of six sides will have straight-sides and will neither grow nor shrink, as shown in figure 2.22. A shrinking grain will gradually lose sides until it reaches the minimum number of three which will all disappear together as the grain itself eventually disappears, figure 2.24. The average number of sides per grain remains at six throughout this process, so that as a grain goes from five to four to three sides, other grains acquire the extra sides: but when a three-side grain disappears, it takes these three sides, which are also three sides of other grains, with it.

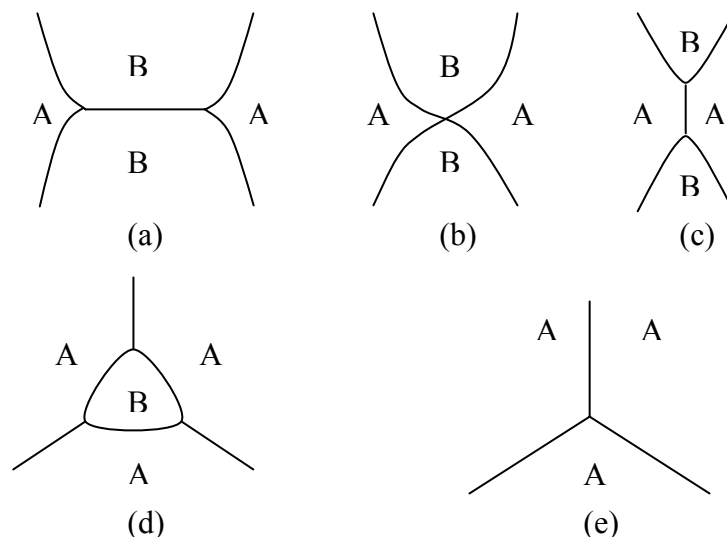


Figure 2.24. *The change of grain size in grain growth. (a), (b) and (c) show the sequence by which grains B lose sides, whereas grains A gain them. (d) and (e) show the disappearance of grain B, together with sides from grains A.*

2.1.2.2. *ADVANTAGES OF MICROWAVE SINTERING AND CHALLENGES THAT MICROWAVE SINTERING FACES AND THE CURRENT AVAILABLE TECHNIQUES APPLIED IN MICROWAVE SINTERING*

2.1.2.2.1. Advantages of Microwave Sintering

Since the early 1970s microwave heating has been used as a means of sintering ceramics. This method is fundamentally different from that in conventional furnaces in which heat is generated internally by the interaction of microwaves with the materials in microwave furnaces while in conventional furnaces materials are heated by thermal radiation. Consequently, it has the capacity for volumetric heating of material and therefore displays a different temperature profile from conventional heating, namely an inverse temperature profile of the hotter centre and colder surface, which makes it to have many benefits such as lower energy consumption and process time, rapid heating and selective heating etc, as seen below.

Lower energy consumption and process time

The reason that microwave heating is fundamentally different from most conventional heating techniques lies in its volumetric heating. This is because microwave is directly deposited in the materials, causing greater energy efficiency and leading to less time required to sinter the materials. As a result, energy consumption can significantly reduce [1, 2, 80].

Rapid heating

Volumetric heating can lead to rapid heating. This will bring ceramic sintering many benefits. This is because rapid heating can restrain grain growth in sintering, producing ceramics with fine microstructures, which improve the mechanical properties. Its important application is to make nano-structural ceramic and composite materials. For example, Yu. Bykov *et. al.* obtained nano-structural titanium oxide by

microwave sintering and the results showed the microhardness of microwave sintered samples was higher than that of the conventionally sintered samples [81].

Selective heating

The third benefit of microwave heating is related to its selectivity, which can provide concentration of energy deposition in the desired region or in phase in a mixture[82-84]. This is because materials with different dielectric losses have different microwave adsorption ability. In a composite material, more energy deposition concentrates on the components with higher dielectric losses. One of applications of the selective heating is in efficient control over the microstructure and properties of ceramics. For example, Li *et. al.* used microwave processing to heat treat a TiC/Si₃N₄ ceramic composite and found that the strength degradation from thermal shock was substantially recovered. The mechanism of strength recovery was that microwave radiation, which caused selective heating of TiC particles, enhanced the reaction of grain boundaries, and resulted in the sintering of microcracks around TiC particles [82].

Inverse temperature profile

Since microwave power is directly deposited into the ceramic, the surrounding air remains cooler than the body, which can result in the creation of an inverse temperature profile with time, *i.e.* a hotter interior than the surface while conventional heating relies on thermal conduction and radiation to transport heat from the surface of the ceramic to the centre of the body. The magnitude of the temperature profile of microwave heating is dependent on many factors such as power level, electric field distribution and the properties of sintered materials including heat losses, thermal and electrical conductivity, *etc.* The inverse temperature profile in microwave heating will benefit for ceramic sintering compared to that in conventional heating. This is because the inverse temperature profile in microwave heating can make the densification to be completed firstly in the sample centre which is the hottest area in the sintered sample, this keeps pores still open from the centre of the sintered sample to the outside, thus

allowing pores to be driven toward free surfaces more easily compared to that in conventional heating. Hence, this effect can contribute to the achievement of a higher final density in microwave sintering. The inverse temperature profile is good for reaction sintering which involves the reaction of a porous solid matrix with a gas phase, e.g. YBCO high-temperature superconductors. [85, 86]

2.1.2.2.2. Challenges Faced by Microwave Sintering

The control of microwave sintering is more complicated and difficult than that of conventional sintering. One problem is “thermal runaway”, when the temperature of the sample increases rapidly with time. It can lead to melting of the sample or to the formation of the local hot spots, i.e. some regions having a much higher temperature than the rest of the sample. It is a direct result of nonuniformity of the microwave field and of the properties of the sample. Nonuniformity in the microwave field leads to the differences in energy absorption with the sample and therefore to different regions of the sample being heated at different rates. The formation of local hot spots will cause differential densification and to cracking of the sample. Additionally, an inverse temperature profile generated by microwave heating can also cause the same problem if the profile is too sharp.

Accurate temperature measurement in microwave heating is another problem in microwave sintering. It presents more difficulties than in conventional heating. For example, due to interference from the microwave field, the use of a thermocouple in microwave heating can significantly change the heating behaviour of the processed materials [87]. Additionally, the presence of inverse temperature profile during microwave heating will lead to an under-estimation of the central temperature of the sample if surface measurement techniques such as pyrometry are used. Section 2.3 discusses this challenge in much greater detail.

2.1.2.2.3. The Current Available Techniques Applied in Microwave Sintering.

However, microwave heating is based upon the capacity of materials to absorb the microwave energy. For the materials with a high absorption ability, they can be heated easily by microwaves, but for many ceramics such as Al_2O_3 , ZrO_2 , SiO_2 , BN and AlN, at low temperature, it is difficult to heat these materials using 2.45 GHz radiation due to their low microwave absorption. In order to heat them using microwaves, many techniques have been applied recently.

One approach is to use coupling agents which can be added to the materials that can not be efficiently heated with microwave energy. The coupling agent interacts with the microwave and pre-heats the samples. However, the disadvantage for the use of coupling agents is also obvious, due to the contamination from coupling agents.

Another approach is to employ a hybrid heating system. It introduces additional heating sources into the system, for example, the application of susceptors which are microwave-absorbing materials that can convert the energy of electromagnetic waves into heat [88]. The most widely used material as a susceptor is silicon carbide (SiC). Usually, susceptor materials are arranged around the transparent ceramic which pre-heats the sample to a temperature where it starts to couple with microwave power. An advantage of the susceptor is that it can reduce the temperature gradient that exists in the sample, which allows the sample to be heated uniformly, thus achieving high density and quality for the sintered samples without the use of applied pressure during sintering. Using this method, enhanced microstructural uniformity and homogeneity was reported for many bulk materials such as YSZ, Ce-Y - ZrO_2 and pure Al_2O_3 ceramics [11,13,14,15,89,90]. However, this susceptor route has many disadvantages. For example, it is not energetically efficient since energy is wasted heating something other than the sample. Additionally, possible contamination of the sintered sample with the susceptor material, especially in the case of using powdered susceptors which may not be removed during sintering, can be regarded as a serious challenge for the use of susceptors. Furthermore, it is difficult to know the microwave power absorbed by the sample and the susceptors due to the unknown absorption behaviour as a function of temperature of the sample and susceptors.

Recently, a novel kind of hybrid furnace with electrical heating elements has also been applied [59]. Compared to susceptors, this method has many benefits listed below:

- a) Accurate and controllable power input
- b) Microwave deposition only in samples
- c) More uniform temperature distribution in the heated samples
- d) No limit in sample size
- e) No contamination

The first and second benefits can make it easy to control the sintering conditions such as sintering curve and temperature profile, etc, this is because there are two control systems in the control unit which can control the input of microwave and conventional power, respectively. The high qualities of sintered products can be obtained by adjusting the fraction of conventional and microwave power to create uniform temperature distribution within the sintered products. Additionally, it is possible to heat any sample with any size in a hybrid furnace. The use of heating elements avoids the contamination from susceptors.

2.2 MICROWAVE EFFECT

2.2.1. MICROWAVE EFFECT

Microwave enhancements can exist in microwave processing. Here it is necessary to distinguish what is meant by nonthermal versus thermal phenomena. “Thermal” refers to interactions resulting in increased random motion of particles where the kinetic energy statistics of such fluctuations are represented by a single thermodynamic equilibrium distribution. Ordinary microwave heating might fall in this category in many conditions. “Nonthermal” effects refer to interactions resulting in nonequilibrium energy fluctuation distributions or deterministic, time-averaged drift motion of matter (or both) [57].

Generally speaking, enhanced mass transport and solid state reaction rates during the processing of a variety of ceramic, glass, polymer, and other organic or inorganic materials, including lower sintering or reaction temperatures, accelerated kinetics for a wide range of processes in these materials, and reduced activation energies, have broadly been called the “microwave effect”. The latter may therefore be categorised as a “nonthermal” phenomenon.

As Rybakov and Semennov said, “for high-temperature reaction experiments involving thermally-activated chemical diffusion, the common manifestation of the microwave effect is to enhance the process kinetics either by reducing the temperature or the necessary time to complete the reaction” [91].

2.2.2. MICROWAVE ENHANCEMENT

Microwaves have been applied in many fields such as chemistry, medicine, and materials science [3-6,8,92-126]. For example, microwave techniques have been used in a large variety of medical applications, both in treatment and diagnosis [96]. Particularly in materials science, microwave processing is gaining more and more attention.

Microwave heating has for many years been successfully employed for some polymer applications, especially in preheating or continuous vulcanization of rubber and also for crosslinking of thermosets [97]. The utilization of microwave processing has been shown to result in a significant enhancement in reaction rates of thermosets when compared with thermal processing methods; microwave heating has been demonstrated to accelerate kinetics in organic systems. Curing of epoxies and other polymer processes has been enhanced [42, 92,93]; accelerated kinetics in the synthesis of numerous organic compounds have been reported [94]; and accelerated diffusion of ethylene oxide through poly (vinyl chloride) polymer has been observed [95]. In two of these cases reduction in the apparent activation energy and pre-exponential factor for the process was reported. Lewis, *et al*, studied the imidization of poly (amic acid) [93]. The apparent activation energy for the reaction was reduced from 105 kJ / mol for conventional heating to 57 kJ/mol for microwave heating (45% reduction); the pre-exponential rate factor was reduced from 2.7×10^{-10} to $4.4 \times 10^{-15} \text{ min}^{-1}$ (5 orders of magnitude decrease). Similarly, Gibson, *et al.*, reported a reduction in the apparent activation energy for diffusion of ethylene oxide through poly (vinyl chloride) from 57.3 to 28 kJ / mol (51% reduction) and a reduction in the pre-exponential factor from 2.73×10^{-3} to $1.7 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$ (4 orders of magnitude decrease) [95].

Recently, more and more researchers have found that a variety of chemical reactions could be accelerated by microwave irradiation of reactants. The great majority of these reactions not only have been in the solution phase, such as microwave-assisted precipitation, and sol-gel and hydrothermal processes, but also have been in microwave-assisted solid-state synthesis of complex oxides, such as cuprates, vanadates, niobates, ferrites, and lead zirconium titanate [3, 102-116]. For example, Binner, *et al*, used microwave heating to prepare titanium carbide. Reaction rates observed during the microwave synthesis of titanium carbide powder via the carbothermal reduction of the oxide were more than three times faster than those observed during conventional processing at the same temperature. Higher yields were obtained at lower temperatures and shorter times when microwaves were used as the source of energy compared to conventional heating [104]. Vaidhyanathan, *et al*, utilized microwaves to assist the solid synthesis of niobates, titanates; Ti, Ga and V nitrides and lead zirconium titanate. The results showed that microwaves not only

accelerated the reactions but also yielded products of good crystallinity and structure uniformity [109-112].

Specially in ceramic processing, microwave heating could provide unique benefits that conventional furnace heating cannot, such as more precise and controlled volumetric heating, faster ramp-up to temperature, lower energy consumption, and improved quality and properties of the processed materials. Therefore, microwave sintering of ceramics is becoming an emerging technology in which the energy is applied directly to the materials being processed, enabling rapid and efficient sintering. The process has shown high potential for the synthesis of advanced structural, as well as functional, ceramic materials with superior properties unattainable by other means. Despite an apparently simple approach, microwave sintering is, in fact, a complex process that combines the propagation and absorption of electromagnetic waves in the ceramic material, heat transport within the geometric body, and densification. The densification changes both macroscopic shape and microstructural morphology. Microwave processing studies of a range of ceramics have led to reports of materials different from those attained using conventional heating [4-6,8,117-119, 124]. Affected properties under investigation include density, porosity, strength, fracture, toughness, electrical permittivity, thermal conductivity, and grain size. For example, Mantin, *et al* [124] studied the ultrasonic and dielectric characterization of microwave-sintered and conventionally sintered zinc oxide, and found in both cases that there was an increase in the measured permittivity values with decreasing porosity; however, the microwave-sintered samples had considerably higher values. Significantly more densification was observed at intermediate temperature for microwave sintering than for conventional sintering. For example, Cheng, *et al*, used microwaves to sinter aluminium oxynitride (ALON) at 1800°C for 1 hour. The sample was shown to be optically transparent [5]. Fan, *et al*, observed the effects of microwave radiation on ilmenite flotation and found that microwave radiation pre-treatment is an effective method to modify ilmenite surface properties and improve ilmenite floatability [119]. After exposure to microwave radiation for a short time, ilmenite recovery was increased by about 20%. The specific surface area of imenite samples underwent a significant change with microwave exposure time; also a new phase was observed. Microwave exposure speeded up the oxidation of

ferrous ions to ferric ions on the ilmenite surface and resulted in an enhancement of oleate ion adsorption and therefore improved ilmenite flotation behaviour [119].

Moreover, microwave processing of ceramics has also been demonstrated to enhance sintering and grain growth. It has been noted that materials sintered by microwave heating display markedly higher densities for a given reaction temperature and time than do conventionally treated samples, the effect being most evident at low temperatures/sintering densities as shown in figure 2.25 [8]. Sintering accelerated in alumina, zirconia, alumina-zirconia composites and silicon nitride has been reported widely [3-6,8]. For example, Janney, *et al*, found that the kinetics of grain growth were greatly increased by 28 GHz microwave anneals; e.g., the grain growth rate at 1500°C in the microwave furnace was the same as the rate at 1700°C in the conventional furnace; also, the activation energy for grain growth was reduced by the microwave anneal from 590 KJ / mol (conventional) to 480 KJ / mol (microwave) [127]. The magnitude of this temperature differential to achieve a given sintered density is often used as a measure of the enhancement caused by microwave processing. Temperature differentials as high as 400°C have been reported [128]. The magnitude of the differentials depends on the material being processed and on the frequency of the microwaves being used. Samuels, *et al* [8], through a comparative study of microwave and conventional sintering of a series of alumina / zirconia compositions, reported that microwave heating enhanced the densification process. Microwave-sintered materials tended to have larger grain sizes, as was expected from their greater densities. Through the adaptation of high-temperature sintering dilatometer for use in microwave environment, an *in situ* monitoring of the sintering process, it was observed that the microwave enhancement of the sintering process was increased for more lossy material compositions, raising the possibility of localized heating. The initial dilatometer results also suggested that the microwave enhancement might be a result of a reduction in the activation energy for grain boundary diffusion. Nightingale, *et al*, [116] sintered 3 and 8 % yttria-zirconia ceramics by employing microwave and conventional heating. Microwave heating enhanced the densification processes occurring during constant-rate heating for both materials. No change was found in the grain size-density relationship for 8 mol% yttria partially stabilised zirconia. However, a small, but statistically significant shift

favouring densification was found for the 3 mol% yttria-zirconia. They thought that the difference in the responses of the two materials might be due to the differences in the activation energy for grain growth and grain-boundary mobility.

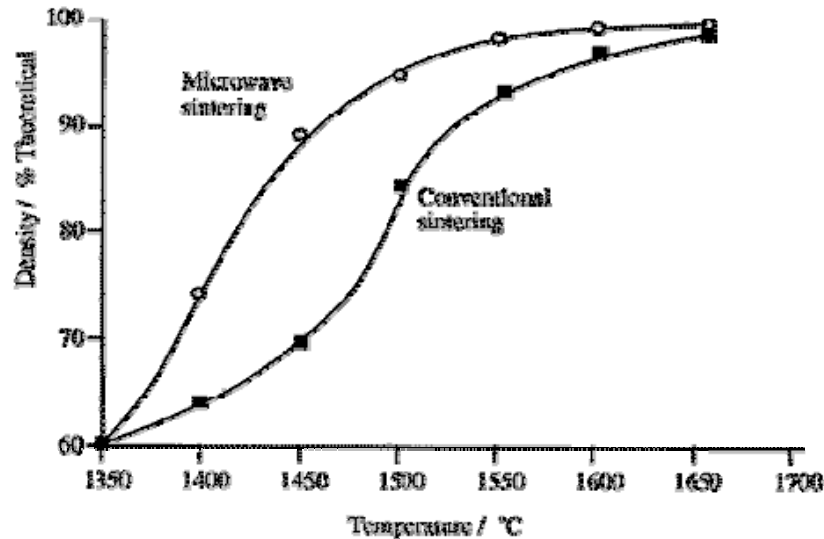


Figure 2.25. Microwave and conventional sintering densities as a function of temperature[8].

Besides sintering, many other solid state thermal processes have been studied in microwave furnaces and compared to conventional processes, for example, some research groups have reported microwave-enhanced joining of ceramic parts [120-124].

Additionally, it was recently found that a wide variety of compacted metal powder and ordinary commercial powder metal compacts could couple effectively with microwave fields and be synthesized or sintered at least as well as or better than conventional heating. Gedevarishvili, *et al*, [118] have demonstrated that microwave coupling efficiency of metals was greatly increased by increasing the temperature of intermetallics and alloys. This was achieved by starting with a hybrid method in which an external susceptor was used to trigger the reaction. Once the metal material was heated to a “critical” temperature, enhanced microwave absorption became sufficient to cause self-heating, and the susceptor could be removed. As microwave energy absorbed by the metal material increased, the temperature of the metal material

also was elevated. The same result also was achieved in a pure microwave system but with slower heating rates.

2.2.3. THE NATURE OF THE “MICROWAVE EFFECT”

In the past, the “microwave effect” has been the source of significant controversy, partly due to the lack of a credible and verifiable theoretical explanation, or failing to observe any resolvable reaction or transport rate enhancements. For example, Fathi, *et al.* attributed the enhanced diffusion to increased vibrational frequency of the ions caused by the electric field of the microwave radiation [126]. Another theory that the “microwave effect” would be an excitation to a non-thermal phonon distribution in the polycrystalline lattice was initially proposed by Booske *et al.*, [129]. However, calculations based on the phonon kinetic (Boltzmann) equation indicate that these phenomena will be negligible for the microwave field intensities. A later theory based on quasi-static polarization of the lattice near point defects was also put forward to explain the effect. But the fate was the same.

As Freeman *et al.*, said, “If microwave heating is perceived as a pure thermal process (by rapid equilibration of microwave energy to thermal energy of the material), then it is difficult to explain how microwave and conventional furnace heating can result in markedly different reaction rates. The various explanations attempted for these experimental observations fall into one of two classes: (1) nonequilibrium thermodynamics, and (2) “nonthermal” phenomena [58, 130].

Most recently a theory was developed by Rybakov and Semenov to explain the “microwave effect” [60, 131]. They suggested that the observed effects arise from the ponderomotive (time-averaged, non-zero) action of the high-frequency electric field on charged vacancies in the ionic crystal lattice, namely, it is the driving force that is affected. The theory can plausibly explain the experimentally observed enhancement of mass transport processes in ionic crystalline solids under the action of high-frequency (HF) electromagnetic fields such as microwaves. It is based on the ponderomotive effects that occur due to the non-linear interaction of the HF electric field with the space charge induced by it within the crystal near its surface. Due to the

action of the tangential component of the field in the near-surface amorphized layer, where the vacancy mobility is greater than in the bulk, the ponderomotive effects were found to be of sufficient strength to manifest themselves in the experimental conditions. They suggested that the flux of vacancies of each sort is determined by diffusion and drift:

$$\mathbf{J}_\alpha = -D_\alpha \nabla N_\alpha + D_\alpha N_\alpha \left(\frac{e_\alpha}{kT} \right) \mathbf{E} \quad (2.74)$$

Where the subscripts are introduced to distinguish vacancies of different sorts, $\mathbf{J}_\alpha$ is the flux density, D_α is diffusivity, e_α is the electric charge, N_α is the dimensionless (normalized to the density of sites in the crystalline lattice) concentration of vacancies of sort α , $\mathbf{E}$ is the vector of the electric field and the vacancy mobility is expressed with the help of Nernst-Einstein relation. The velocity V of deformation, i.e. of crystal surface displacement, is used for a measure of mass transport. It is connected with the total vacancy flux density, J , on the surface: $V = -\mathbf{n} \cdot (\mathbf{n} \cdot \mathbf{J}|_s)$. Here $\mathbf{J}|_s$ is the value of the crystal surface and $\mathbf{n}$ is the outward unit normal to the surface. For simplicity, a crystal was considered to have two sorts of vacancies with opposite charges, $e_{1,2} = \pm e$, and equal diffusivities, $D_{1,2} = D$. In this case, the slowly varying (quasistationary) charge separation field is absent, and the quasistationary components of concentrations of vacancies of two sorts are equal. Therefore, the problem of quasistationary vacancy flow for the total averaged vacancy concentration $N = \sum [N_\alpha]$ can be formulated easily, and the total averaged vacancy flux can be described as follows:

$$\mathbf{J} = \sum \mathbf{J}_\alpha = -D \nabla N + \left(\frac{\omega}{kT} \right) D \langle \rho \mathbf{E} \rangle \quad (2.75)$$

Here ω is the vacancy volume, $\rho = \sum e_\alpha N_\alpha / \omega$ is the density of electric charge (oscillating with the field frequency) associated with vacancies and the angular brackets denote averaging over the period of the HF field. The second term on the right of the equation expresses vacancy drift under the action of the averaged ponderomotive force.

The recent theory of averaged pondermotive action of microwave fields in solids was expanded to describe quasistationary ionic currents driven by that action [125]. Several limiting cases were explored in detail and in all cases the effect was shown to depend on the interfacial properties of the ionic crystal. Some experimental results on the dynamics of the microwave-induced currents in AgCl and NaCl were presented. Agreement between experiment and theory has provided further and stronger evidence for the general validity of the theoretical model [57, 130].

2.2.4. THE EXPERIMENTAL WORK THAT HAS BEEN DONE TO EXPLAIN THE “MICROWAVE EFFECT”

In order to explain the “microwave effect”, research about the diffusion in materials during microwave heating has been carried out. The most straightforward experiment was to follow the diffusion of a particular ionic species into the bulk of a single crystal. Janney *et al.* suggested using tracer ions that are isotopes of the ions that comprise the material chosen for study [127, 132]. This would guarantee that the dielectric properties of the doped and undoped regions would be as similar as possible. Aluminium oxide (sapphire) was chosen as the matrix material because Janney *et al.* considered that previous studies of sintering and grain growth had reported that a “microwave effect” was obtained in this system.[132] The stable isotope ^{18}O was chosen as the diffusing species. Also, the doped and undoped regions of the sample had similar chemical and dielectric properties. Their experimental results demonstrated that (1) volume diffusion of ^{18}O in alumina was enhanced by heating in a 28 GHz microwave furnace; (2) the apparent activation energy for volume diffusion was reduced by 40% from 650 to 390 KJ / mol; the pre-exponential factor was reduced by five orders of magnitude from 9.7×10^{-2} to $3.8 \times 10^{-7} \text{ (m}^2\text{s}^{-1}\text{)}$; (3) the results helped to explain the accelerated kinetics observed during sintering and grain growth in the alumina, zirconia, and silicon nitride ceramic systems and (4) the results were consistent with those reported previously for microwave acceleration of ion-exchange in silicate glasses.

Based on the model proposed by Rybakov and Semenov, Freeman *et al* considered that, in effect, the microwave field induces a nonequilibrium concentration of vacancies in a small region near the surface of the ionic crystal [130]. Mass flow is required to reach this nonequilibrium condition and because the vacancies are charged, there is also an induced charge flow. All of the microwave-enhanced processes could be characterized by a general relation,

$$RATE = (DRIVING FORCE) \times (TRANSPORT COEFFICIENT) \quad (2.76)$$

For diffusion processes, the coefficient involves the carrier concentration, c , and the microscopic diffusion coefficient, D , which for conditions near thermal equilibrium follow an Arrhenius-type behaviour,

$$D = D_0 \exp\left(-\frac{Q}{kT}\right) \quad (2.77)$$

Where Q is the activation energy for diffusion and kT is the thermal energy. Some experiments were designed to test for microwave enhancement of vacancy transport processed in NaCl. Freeman, *et al*, reported the results comparing experimentally measured currents in sodium chloride (NaCl) crystals in the presence and absence of intense microwave fields, the currents being ionic in nature. They considered that the ionic current (actually charge flux) through a ceramic sample induced by an applied bias voltage is [130]

$$J_i = \left(\frac{D_i c_i}{kT}\right) z_i^2 e^2 \left(\frac{V_{bias}}{\delta}\right) \quad (2.78)$$

where i refers to the most mobile charged species, J is the flux, c is the concentration, D is the diffusion coefficient, kT is the thermal energy, z is the valence, e is the electron charge, V_{bias} is the applied bias voltage and δ is the crystal length. The results demonstrated that high-power microwave fields could enhance mass transport in ionic crystalline solids, however intrinsic vacancy mobility was not enhanced by microwave fields. Some numerical simulations were also provided and showed that the results were in good agreement with qualitative predications of a non-linear

ponderomotive force (pmf) model. This force arises at any abrupt nonuniformity in medium transport properties, such as free surfaces, grain boundaries, or amorphous-crystalline structure interfaces. Numerical simulations have provided additional insight into the details of this phenomenon. In particular, illustrative simulations of NaCl showed that opportunities to observe and take advantage of enhanced mass transport due to strong microwave fields will depend on the application and physical circumstance. Similar conclusions were drawn by Wroe and Rowley [59] in the UK based on the sintering of yttria stabilised zirconia (YSZ). They found that an enhancement in densification when using microwaves was consistent with a dependence on the electric field experienced by the material.

Although the model proposed by Rybakov and Semenov can explain enhanced diffusion or solid-state reaction rates with microwave heating when compared with conventional heating, it can not solve the problem of the “microwave effect” in non-ionic systems such as polymers (assuming that it is the same effect which is operational in these systems) [104], also it can not account for the magnitude of the temperature differential observation caused by microwave processing when compared with conventional heating. The interaction between microwaves and materials not only depends on the structure and properties of materials such as on the dielectric properties and the porosity of the material, and on the shapes and the sizes of material particles and the pores, but also depends on the dopant, defects, atoms, ions, molecules and valency electrons. Thus it is quite possible that multiple models will be needed to explain the effects.

2.3. TEMPERATURE MEASUREMENT

2.3.1. TEMPERATURE MEASUREMENT TECHNIQUES USED DURING MICROWAVE PROCESSING

The majority of temperature measurement techniques used during conventional heating, such as radiation pyrometer, optical-fibre thermometry, or contact measurement using a thermocouple have been used during microwave processing with suitable modification. The main features of these techniques are listed in the table 2.3.

Table 2.3. Comparison of Temperature Measurement Techniques during Microwave Processing [87].

	Monochromatic Radiation pyrometer	Two-colour radiation pyrometer	Optical-fibre thermometer	Thermocouple
Measurement range (°C)	0-2800	400-4000	0-1900 (monochromatic) 500-1900 (two-colour)	0-1600
Accuracy	Moderate to high	High to excellent	Excellent	Good in conventional furnace; Unproved in microwave furnace
Problems	Large minimum spot size; sensitive to magnitude of emissivity	Sensitive to slope of emissivity	Delicate probe; cannot interchange probes readily; contamination of; probe	High temperature not available; perturbs microwave field; contamination of sample

2.3.2. THE CHALLENGE THAT TEMPERATURE MEASUREMENT IS FACING IN MICROWAVE PROCESSING AND IT'S ALTERNATIVE

Although the above temperature measurement techniques have been used in microwave processing, their temperature measurement accuracy has not been ascertained. For example, all the above-mentioned microwave effects in section 2.2 rely for their validity on accurate temperature measurement in a microwave field.

Because processing of ceramic materials and some chemical reactions are governed by temperature history, proper *in situ* measurement is crucial. In ceramic processing, a thermocouple-based temperature-sensing system is common for conventional heating. Thermocouple use in microwave processing is also common but may be problematic, because its presence within the cavity may affect the heating process and the measured temperature [87]. Thermocouples can only be used if shielded from the microwaves by a metal tube, often platinum to withstand the high temperatures generated during processes such as sintering. In addition, to prevent electrical discharge between the tip of the thermocouple and the surface of the component, then either an electrically insulating layer needs introducing between thermocouple and sample or a small air gap must be left. Either approach reduces the sensitivity and accuracy of the temperature measurements. Pyrometry is often used to avoid the above problems with thermocouples, however this technique again monitors surface temperatures and, as is well known, these can be significantly different from internal temperatures.

A temperature measurement system that is effective in a microwave field, should not perturb the microwave field, be affected by the field or significantly disturb the thermal distribution within the sample [87]. One system that comes close to achieving these goals is the use of optical thermometry in which the temperature of the sample is sensed by either a microwave transparent black body tip mounted on a sapphire rod or by using a sapphire rod as a light pipe and monitoring temperature by pyrometry. In either case, the probe can be used to monitor either surface or internal temperature, the latter by inserting it into a hole drilled into the sample. Since high purity sapphire has an extremely low dielectric loss, it is effectively immune to microwave radiation, although the black body tip can interact with strong electric fields. Additional disadvantages are the extremely brittle nature of the sapphire rods, the high capital cost of the system, and the difficulty in envisaging how the technique could be used for the production of industrial-scale quantities of materials.

Chapter 3

EXPERIMENTAL

3.1. EXPERIMENTAL EQUIPMENT

3.1.1. TEMPERATURE MEASUREMENT DEVICES

3.1.1.1. *THERMOCOUPLE*

Thermocouples are among the easiest temperature sensors widely used in science and industry. A thermocouple is a thermoelectric temperature sensor that consists of two dissimilar metallic wires, e.g., one chromel and one constantan. These two wires are connected at two different junctions, one for temperature measurement and the other for reference. The temperature difference between the two junctions is detected by measuring the change in voltage (electromotive force, EMF) across the dissimilar metals at the temperature measurement junction.

Thermocouples are cheap, interchangeable, have standard connectors and can measure a wide range of temperatures. Additionally, a thermocouple can be used to monitor local temperature, because it is easy to insert into a small volume. Because of these advantages, thermocouples are also used in microwave processing to monitor temperature, however they need shielding from the electromagnetic field and so are inserted into a thin wall, narrow metal tube prior to use.

3.1.1.2. PYROMETRY

A pyrometer consists of an optical system and detector. The optical system focuses the energy emitted by an object onto the detector, which is sensitive to the radiation. The output of the detector is proportional to the amount of energy radiated by the target object (less the amount absorbed by the optical system), and the response of the detector to the specific radiation wavelengths. This output can be used to infer the objects temperature. The emissivity, or emittance, of the object is an important variable in converting the detector output into an accurate temperature signal.

The device used was a Minolta/Land Cyclops 152 pyrometer, which is a portable infrared thermometer designed for non-contact temperature measurements. It features a $1/3^\circ$ measurement angle and can measure temperatures from 600°C to 3000°C .

3.1.1.3. OPTICAL FIBRE THERMOMETRY (OFT)

The optical fibre thermometry (M10 and M100, Luxtron, USA) is a non-contact or contact temperature measurement instrument. In the former mode, the system consists of a narrow diameter sapphire rod that acts as a light pipe to gather the radiation from the target to a photo detector in the electronics unit. The photo detector converts the light energy into an electrical signal which is then digitised. This signal is converted into a temperature value using Planck's radiation equation. It requires knowledge of the emissivity of the material, however, in the contact mode, the same sapphire light pipe has a very thin (less than $10\text{ }\mu\text{m}$) coating of refractory precious metals at the end that turns it into a black body. The temperature of the latter is then sensed by the instrument, removing the need to know the targets' emissivity. The black body tip can interact with the microwave field if the latter is too intense, however for multimode applicators, such as used in the current work, this is not a problem.

3.1.1.4. THERMAL IMAGING CAMERA

ThermoVSIONTM A40 (Boston, USA) is a thermal imaging camera with a higher than 320×240 pixels, a temperature range of -40°C to 2000°C , an accuracy of $\pm 0.1^\circ\text{C}$ and five measurement modes including: spot, line, area, isotherm and difference, which measures and images the emitted infrared radiation from an object by the fact that radiation is a function of object surface temperature.

3.1.2. THE EQUIPMENTS OF CERAMIC SINTERING AND CERAMOGRAPHIC PREPARATION

The hybrid microwave furnace, which was supplied by C-Tech Innovation Ltd, consisted of a magnetron, waveguide, cooling system, circulator, microwave tuner and hybrid microwave cavity (an applicator). The latter, figure 3.1, consisted of a rectangular metallic box, a stirrer and alumina fibre insulation materials. It also contained six MoSi₂ heating elements. The magnetron supplied up to 1.2 kW of 2.45 GHz microwave power. The conventional heating and microwave heating were controlled by separate Eurotherm controllers. The furnace was specially designed to allow both microwave and conventional heating sources to operate simultaneously [61].



Figure 3.1. The applicator of the hybrid microwave furnace

3.1.3. THE EQUIPMENT FOR ANALYSIS OF CERAMICS

3.1.3.1. *X-RAY DIFFRACTOMETER (XRD)*

The X-ray diffractometer was a Bruker D8 model with a quarter-circle eulerian cradle, which is a non-destructive tool to analyze the crystalline phase and basic structure of the materials.

Testing conditions:

1. CuK α radiation was used.
2. All the samples were analyzed at a scan speed of 2°/min.

3.1.3.2. *FIELD EMISSION GUN SCANNING ELECTRON MICROSCOPY (FEG-SEM)*

The Leo 1530VP field emission gun SEM (FEGSEM) is capable of nanometre-scale resolution and equipped with a variable pressure facility and EDAX/TSL Pegasus system allowing simultaneous electron backscattering diffraction and energy-dispersive x-ray analysis.

Testing conditions:

1. Working distance (WD) was 6 mm;
2. The accelerating (EHT) voltage of the electron beam was 5.00 kV.
3. In order to increase the electrical conduction of a ceramic sample, a gold coating was formed on the sample surface by sputtering or evaporating before the sample was tested.

3.2. EXPERIMENTAL PROCEDURE

3.2.1. EVALUATION OF TEMPERATURE MEASUREMENT TECHNIQUES IN MICROWAVE HEATING

3.2.1.1. MELTING POINT MEASUREMENT OF V_2O_5

The melting point of V_2O_5 was employed for temperature accuracy evaluation in microwave heating because of its ability to heat rapidly from room temperature in a microwave environment. The melting point of V_2O_5 powder (Fisher company) measured by DSC is 688.6°C.

Vanadium pentoxide pellets measuring 25 mm in diameter by 16 mm high were prepared using a hydraulic press. Loose vanadium pentoxide powder was also used in the experiments. Before these experiments, the emissivity of V_2O_5 at different temperatures was carried out for the pyrometer.

Temperature measurement devices: a pyrometer (Minolta/ Land Cyclops 152), an optical fibre thermometer in black body mode (M10, Luxtron, USA), and two shielded thermocouples (type R) with 1.5 mm and 3 mm diameters were used to evaluate the melting point of V_2O_5 .

Based on the volumetric heating of microwaves and the resulting higher central temperature, the temperature was measured by inserting the thermocouple and optical fibre thermometer (OFT) probe into the centre of the loose V_2O_5 powder whilst the pyrometer measured the temperature by a narrow hole drilled into the centre of a V_2O_5 pellet. The heating rate was controlled by changing microwave power to avoid thermal runaway and only pure microwave power was used. Normally the experiments looked for the value at which the temperature became constant due to the presence of both solid and liquid phases to get the melting point, figure 3.2.

In order to observe the size effect of the thermocouples and the effect of microwave power on their measurement, two thermocouples with 1.5 mm and 3 mm diameters and four different microwave powers were used in the experiments.

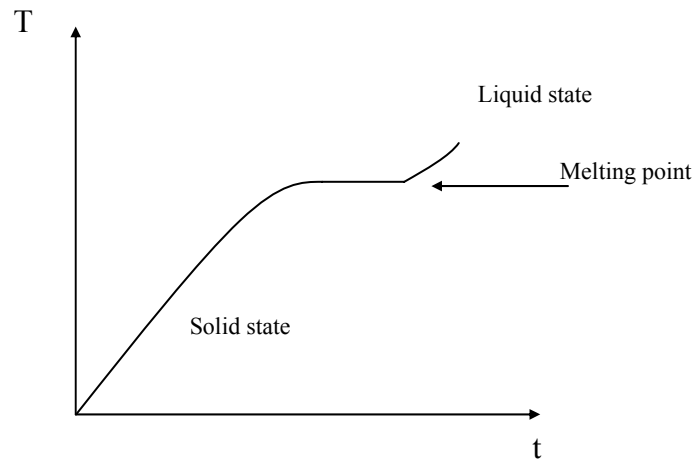


Figure 3.2. Melting point measurement

3.2.1.2. THERMAL RUNAWAY

Some microwave heating experiments that have been done revealed that the use of thermocouples could cause thermal runaway. To investigate this further, pressed samples of zinc oxide, zirconia and alumina pellets measuring 25 mm in diameter by 6.3 mm-12.6 mm in thickness were used in experiments in which the temperature was measured at the centre of the upper surface, figure 3.3, during pure microwave heating

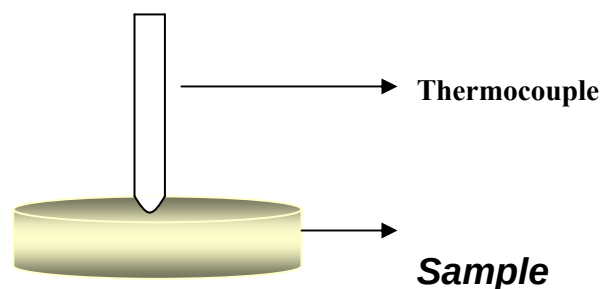


Figure 3.3. The sample being measured by a thermocouple.

Two thermocouples with 1.5 mm and 3 mm diameter were used. The ceramics selected each had a different dielectric loss; ZnO very lossy, ZrO₂ intermediate loss and Al₂O₃, very low loss.

3.2.2. DENSIFICATION STUDIES

3.2.2.1. SELECTION OF MATERIALS

Four different ceramic materials were selected for the sintering experiments, viz zinc oxide (high dielectric loss), yttria stabilised zirconia (YSZ), (medium dielectric loss), alumina (low dielectric loss) and silica (low dielectric loss). In addition, two grades of YSZ, 3 and 10 mol % Y_2O_3 , and two grades of Al_2O_3 , were investigated. Table 3.1 indicates the fundamental properties of ZnO, YSZ, Al_2O_3 and SiO_2 .

Table 3.1. Properties of materials used in this study [133 - 136].

Properties	Materials			
	Alumina	Silica	Zirconia	Zinc oxide
Density / gcm^{-3}	3.5	2.65	5.56(m), 6.10(t), 5.91 (c)	5.606
Melting point / $^{\circ}C$	2015 $\pm$ 15	1477	2715	1975
Specific heat / J/kgK	880		–	500
Relative permittivity at 2.45 MHz	9-10		36.8(c), 46.6(t), 19.7(m) 25(3%YSZ), at 1 MHz	~13
Tan δ at 2.45 MHz	5×10^{-4}	4×10^{-4}	10^{-3} at 1 MHz	0.24

C = Cubic, t = tetragonal, and m = monocline

3.2.2.2. PROCEDURE FOR SINTERING

Sample preparation

Two zinc oxide powders, two 3 mol % yttria stabilised zirconia (3-YSZ) powders, one 10 mol % yttria stabilised zirconia (10-YSZ) powder, two alumina powders and one silica powder were used in the experiments. They consisted of micro-, submicron-

powder and nano-sized powders. Table 3.2 shows the purities and source of the powders.

Table 3.2. The purities and source of the powders

Material	Particle size	Purity	Source
ZnO	Micron	99.9%	Sigma-Aldrich
	Submicron	99.5%	Sigma-Aldrich
3-YSZ	Submicron	99%	HSY-3U, MEL
	Nano		MEL
10-YSZ	Submicron	99%	MEL
Alumina	Nano	99.7%	Sigma-Aldrich
	Nano		Synthesized via sol-gel route
Silica	Nano		Sigma-Aldrich

All the pellets were prepared using a hydraulic press. The binder (poly (ethylene glycol)-block poly (propylene glycol)-block-poly (ethylene glycol), Sigma-Aldrich) was burned out of the samples by heating to 450°C for 2 hours. The green densities of the ZnO and silica samples were ~58% and ~50% TD whilst that of the YSZ and alumina samples were ~44% and ~35% TD, respectively. The size of the pellets is shown in table 3.3 below. The aim is to investigate the effect of the sample size.

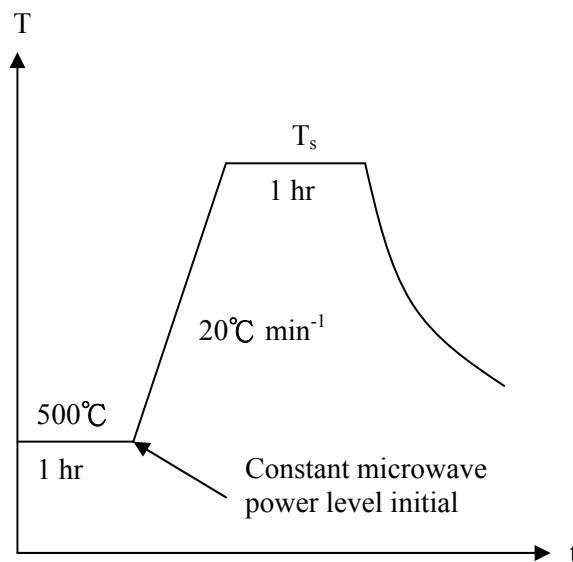
Table 3.3. The sample sizes for different materials used

Diameter / mm	Thickness / mm	Materials
16	5	Zinc oxide, YSZ, alumina and silica
13	5	Zinc oxide
13	3.5	Zinc oxide
13	2.4	Zinc oxide
13	1.2	Zinc oxide
25	5	Zinc oxide

Sintering

Sintering temperature and soaking time were deliberately selected to allow densification to occur and at the same time not to yield full densification during conventional heating so that any change in densification as a result of increasing microwave power was observed. The selection of sintering temperature could be done based on the results of conventional sintering, see section 4.2.1.2. Two different sintering temperatures, T_s , were investigated for each material, as shown in table 3.4. The results revealed that a soaking time of 1 hour would be the best choice to allow the change of density to be observed easily.

The primary aim of the sintering experiments was to expose the samples to varying levels of microwave and conventional power whilst ensuring that they all saw exactly the same temperature – time profile so that direct comparisons between them could be carried out. This is shown in figure 3.4 below.



T – Temperature, t – time and T_s – sintering temperature

Figure 3.4. Sintering curve.

It should be noted that not only were the hold temperature and time maintained precisely but so also were the heating and cooling rates. The heating rate below 500°C below is not shown because the optical fibre thermometers (OFT) used to monitor

temperature could not read below 450°C. Therefore the hold at 500°C was used to ensure thermal equilibrium was reached before the significant part of the experiment began when the microwaves were switched on and the sample heated to the hold temperature for 1 hour. The above temperature-time profile was achieved using fixed levels of microwave power (0, 200, 400, 600, 800, 1000W) and whatever conventional power was needed. (Note: In the initial experiments the top surface temperature was used to control the sample temperature, this was subsequently changed to be the central temperature, see next section).

Table 3.4. Selected sintering temperatures used for sintering experiments

Materials	Approach *	Sintering temperature / °C
Submicron ZnO Sigma-Aldrich	C + n kW mw	680
	PC	
	C + n kW mw	780
	PC	
Micron ZnO Sigma-Aldrich	C + n kW mw	780
	PC	
	C + n kW mw	900
	PC	
Submicron 3-YSZ HSY-3U	C + n kW mw	1100
	PC	
	C + n kW mw	1200
	PC	
Nano 3-YSZ MEL	C + n kW mw	900
	PC	
	C + n kW mw	1000
	PC	
Submicron 3-YSZ MEL	C + n kW mw	1220
	PC	
	C + n kW mw	1260
	PC	
Submicron 10-YSZ MEL	C + n kW mw	1220
	PC	
	C + n kW mw	1260
	PC	
Sol-gel alumina Synthesized	C + n kW mw	1180
	PC	
	C + n kW mw	1260
	PC	
Nano alumina Sigma-Aldrich	C + n kW mw	1400
	PC	
Silica Sigma-Aldrich	C + n kW mw	1000
	PC	

n is 0.2, 0.4, 0.6, 0.8 and 1, respectively.

*: “C + mw is conventional (C) and microwave (mw) hybrid heating; n kW mw is n kW microwave power level”.

3.2.3. THERMAL GRADIENT MEASUREMENT

a. The use of two OFTs

Throughout each experiment as described in section 3.2.2, the temperature was monitored using OFT at two locations, the centre of the sample (via a narrow hole drilled into the sample) and the edge of the sample. This allowed any temperature gradient experiments to be determined.

b. The use of a thermal imaging camera

The samples were sintered according to the temperature-time profile shown figure 3.4. At the same time, the surface temperature gradients were measured by a thermal imaging camera as shown in figure 3.5, and during measurement, the surface thermal imaging of the sample was obtained by focusing in on the sample surface through a metal tube on the furnace and the adjustment of emissivity of the sample and background temperature. The central temperature of the sample was controlled by an OFT and the edge temperature measured by another OFT was regarded as a reference temperature for this camera. In order to decrease the effect of radiation from the elements, the samples were placed in an insulation box with a window.



Figure 3.5a. An imaging camera during measurement.

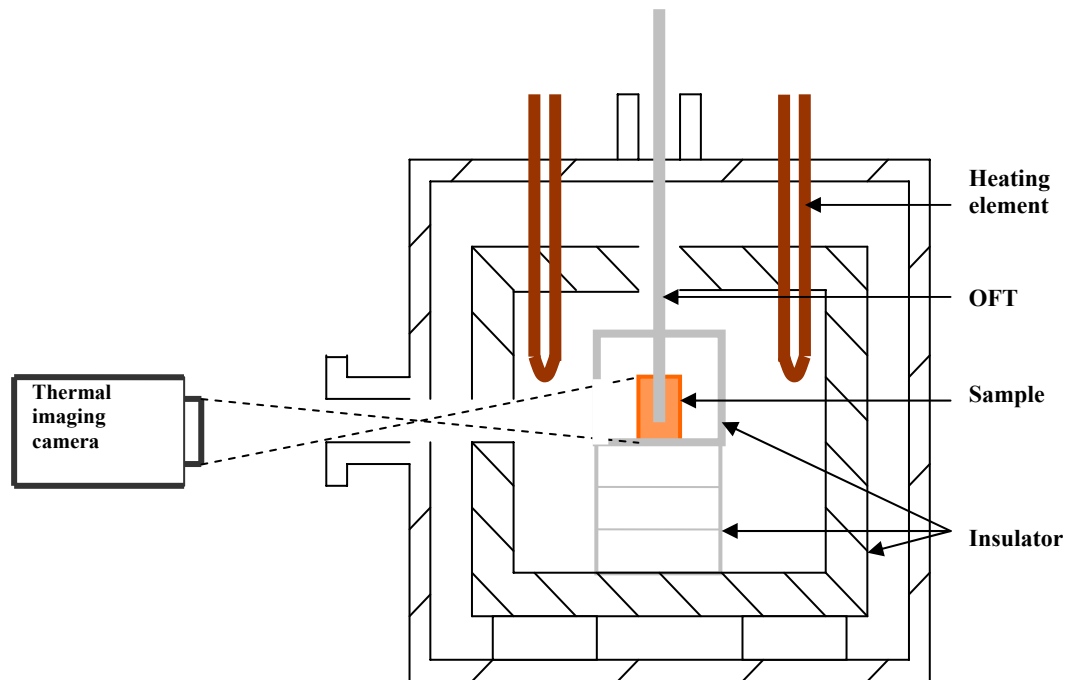


Figure 3.5b. Schematic of an imaging camera during measurement.

c. The examination of grain size

The grain sizes cross the samples were also used to check the temperature gradient from the sample centre to the surface, see section 3.2.6.

3.2.4. GRAIN GROWTH

In order to observe the grain growth under varying microwave power levels, it was necessary to prepare fully dense pellets with small grain sizes. These ZnO pellets with densities higher than 98% of TD and grain sizes smaller than 2 μm were prepared by the two-step sintering method [137]. Then these pellets were annealed using pure conventional heating and hybrid heating with 1000 w microwave power at different temperatures such as 900°C, 1000°C, 1100°C, 1150°C and 1200°C for 1, 3 and 5 h. Only ZnO was used for this work due to the hybrid sintering furnace being limited to an upper temperature limit of 1450°C.

Samples were prepared for electron microscopy using standard ceramographic techniques, see section 3.2.6. Grain sizes were determined using the Linear-Intercept

method [138] and image processing with a computer was used for the analysis of grain size distribution. The results from different parts of the specimens were determined.

3.2.5. IN SITU MEASUREMENT OF SINTERING SHRINKAGE USING A DILATOMETER

A dilatometer was used to measure the shrinkage of the samples during sintering as described in section 3.2.2.. The dilatometer used to measure sample shrinkage was constructed to avoid its operation being affected by microwaves and to minimize its effect on the microwave field distribution within the sample space, figure 3.6. For each sintering experiment, two runs were required. The first run was the actual sintering process whilst the second was a calibration experiment using a fully sintered sample in place to remove the error resulting from the thermal expansion of the samples.

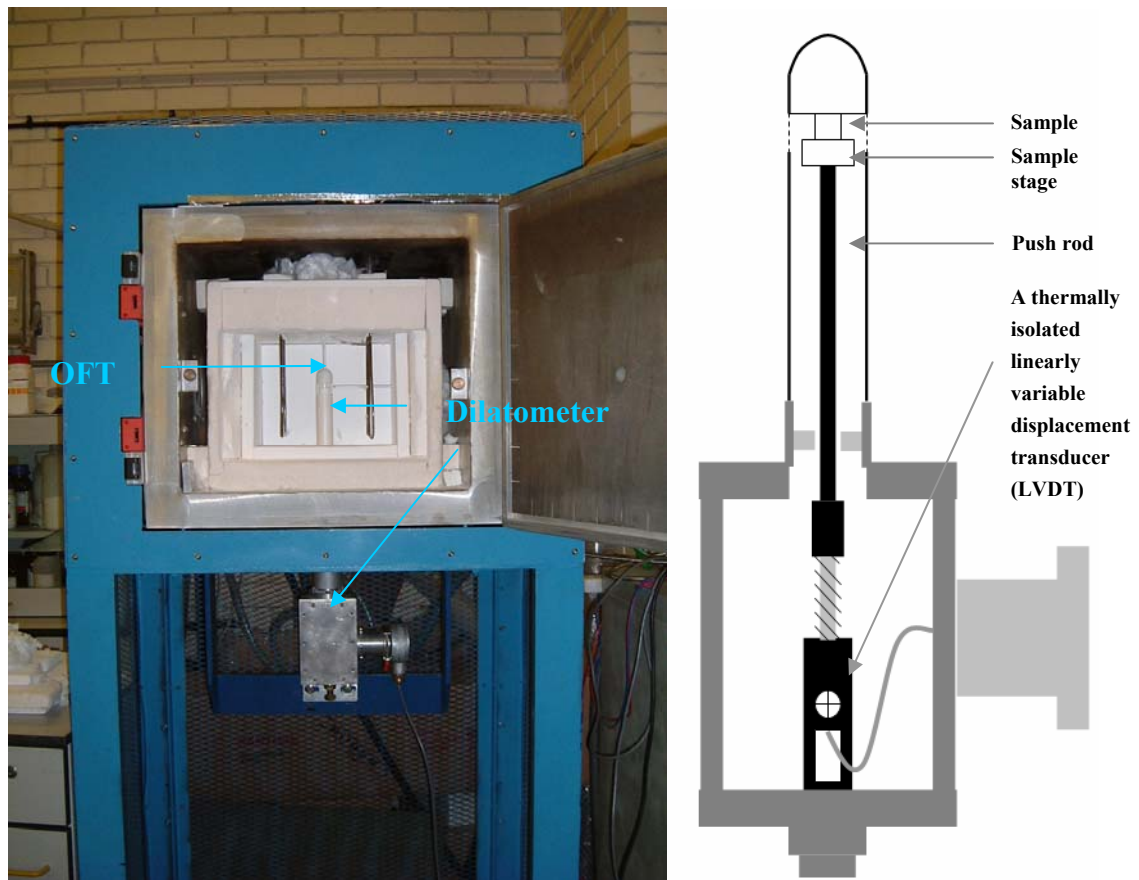


Figure 3.6. The dilatometer and the applicator of the hybrid microwave furnace and the schematic of the dilatometer.

3.2.6. CHARACTERIZATION

The particle sizes of powders and the microstructures of the sintered specimens were observed by field emission gun scanning electron microscopy (FEGSEM) whilst the grain size of the sintered specimens were studied by both FEGSEM and X-ray diffraction (XRD). Additionally, the phases of the sintered specimens were analysed by XRD.

Ceramographic preparation was carried out according to the flow chart as shown in figure 3.7.

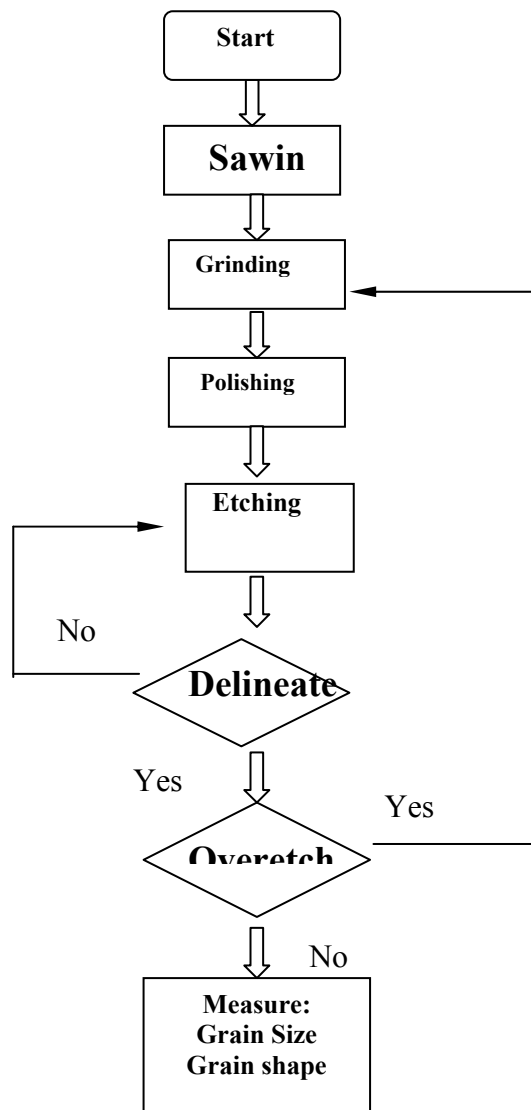


Figure 3.7. The flow chart of the ceramographic preparation.

3.2.6.1. FIELD EMISSION GUN SCANNING ELECTRON MICROSCOPY EXAMINATION

The microstructure of the specimens was observed by field emission gun scanning electron microscopy (FEGSEM) on both fracture and polished selected surfaces.

The grain size was determined by the Linear-Intercept method [138] using micrographs of polished surfaces. This method can measure the mean grain size from the number of grains (intercepts) or grain boundaries (intersections) that intersect one or more lines of known length superimposed on a field of view or micrograph. The mean grain size was calculated by the equation,

$$D = \frac{L \times A_1}{M \times N} \quad (3.3)$$

where D is the equivalent mean grain diameter, L is the length of superimposed lines, A_1 is the shape correction factor, 1.00, M is magnification (dimensionless) and N is the quantity of intercepts or intersections.

Additionally, the grain size can also be obtained by X-ray diffraction, see the following.

3.2.6.2. X-RAY DIFFRACTOMETER EXAMINATION

A second estimate of the grain size was determined using the Scherrer equation [139],

$$D = K\lambda/(\beta\cos\theta), \quad (3.2)$$

where D is grain size, K is a constant (0.89), β is the pure x-ray diffraction broadening and λ is the wavelength (usually 1.542 Å for Cu $K\alpha_1$).

3.2.6.3. DENSITY MEASUREMENT

Green densities were obtained by measurement of the dimensions and the sample mass. The densities of the sintered samples were measured using the Archimedes method:

$$\rho = \frac{M_s \cdot \rho_l}{M_s - M_l} \quad (3.1)$$

where ρ is the specific gravity of the solid, M_s is the weight of the solid in air, ρ_l is the density of the liquid (distilled water) and M_l is the weight of the solid in liquid.

Chapter 4

RESULTS

4.1. EVALUATION OF TEMPERATURE MEASUREMENT TECHNIQUES DURING MICROWAVE HEATING

4.1.1. MELTING POINT MEASUREMENT OF V_2O_5 IN MICROWAVE HEATING

Table 4.1 shows the melting point of V_2O_5 measured by three different techniques in microwave heating; OFT showed very accurate temperature measurement.

Table 4.1. Melting point of V_2O_5 measured by three different techniques in microwave heating.

Approach	Melting point / °C in microwave heating	ΔT / °C
OFT	687 ± 1	1
Pyrometry	661 ± 2	28
Thermocouple Ø1.5 mm	575 ± 4	125
Ø3 mm	526 ± 7	173
Measured by DSC	688.6 ± 0.5	–

By measuring melting point of V_2O_5 , it was found that the measurement errors of a type R thermocouple with 3 mm diameter in microwave heating increased with increasing microwave power, as seen in figure 4.1.

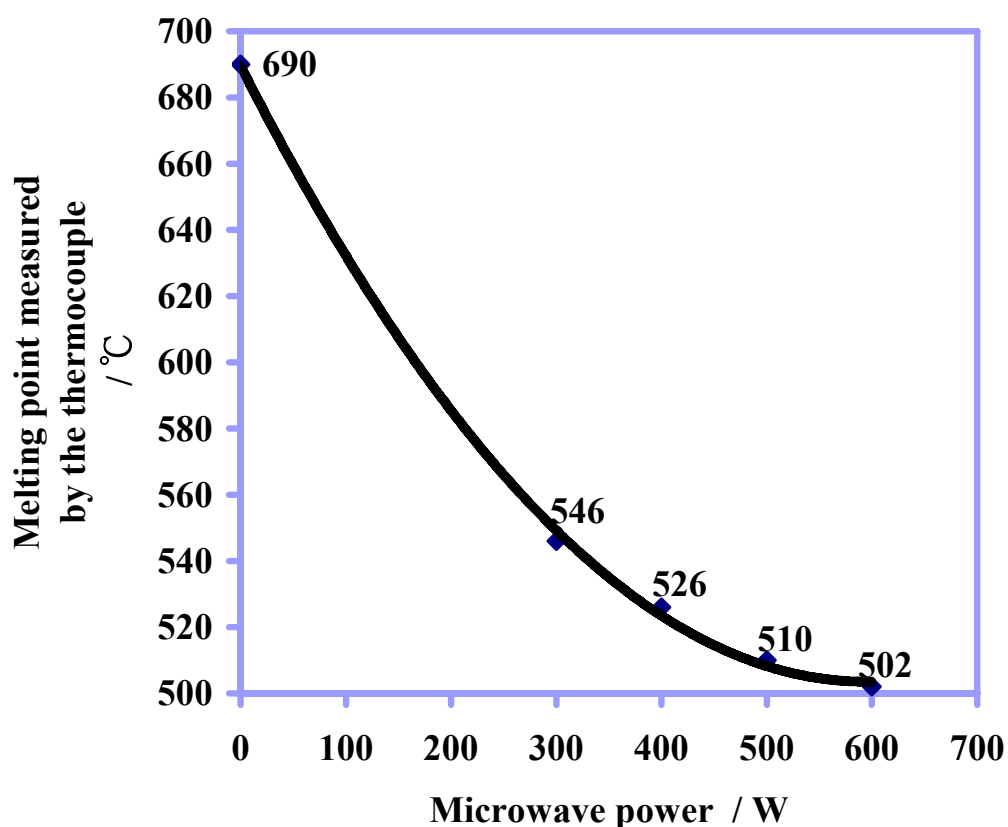


Figure 4.1. The melting point of vanadium oxide measured by the type R thermocouple with 3 mm diameter at different microwave power levels.

4.1.2. THERMAL RUNAWAY

Figure 4.2 shows thermal runaway observed when the temperature of the zinc oxide sample was greater than 400°C for the experiments involving pure microwave heating and temperature measurement by a 1.5 mm diameter type R thermocouple (1.5RT) touching the sample

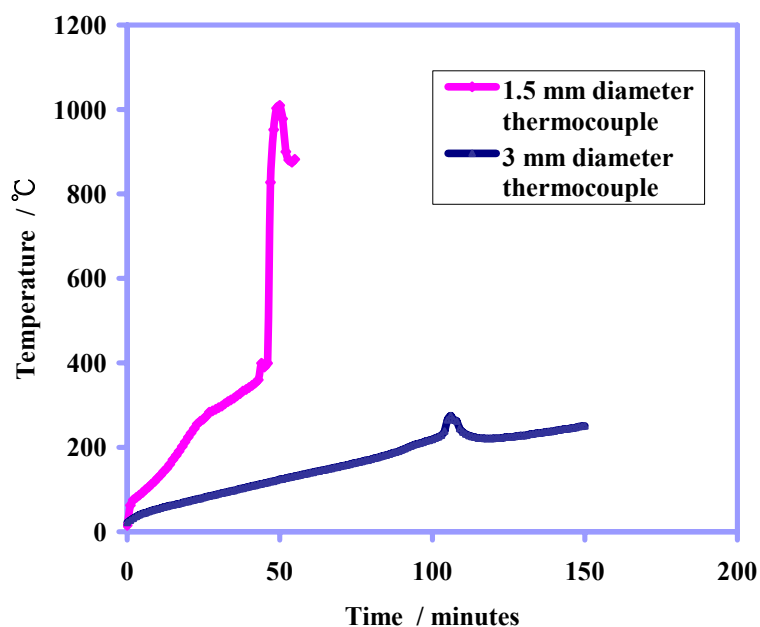


Figure 4.2. Pure (900 W microwave) heating curve of zinc oxide.

Figure 4.3 shows how the V_2O_5 pellet only melted locally during microwave heating when the 1.5 mm diameter thermocouple was in contact with the sample, further revealing the enhanced local microwave field around the thermocouple tip. But no thermal runaway was observed for the 3mm diameter thermocouple (3RT).



Figure 4.3. The melted region on the V_2O_5 pellet due to the focusing of the microwaves by the thermocouple during microwave heating.

Figure 4.4 and 4.5 show that thermal runaway was caused during microwave heating of zinc oxide, zirconia and alumina and that temperatures causing thermal runaway by discharging varied with distance between the thermocouple (1.5RT) and sample in

these materials. The shorter the distance, the lower the temperature to cause thermal runaway.

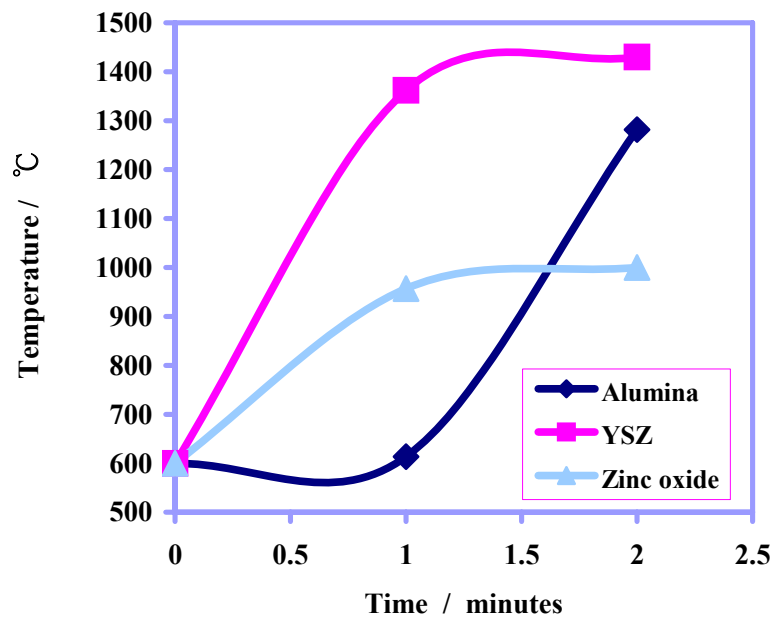


Figure 4.4. Pure (900 W) microwave heating curves of zinc oxide, YSZ and alumina with 1 mm gap between sample and thermocouple (1.5RT), showing critical temperature for thermal runaway temperature caused by discharging.

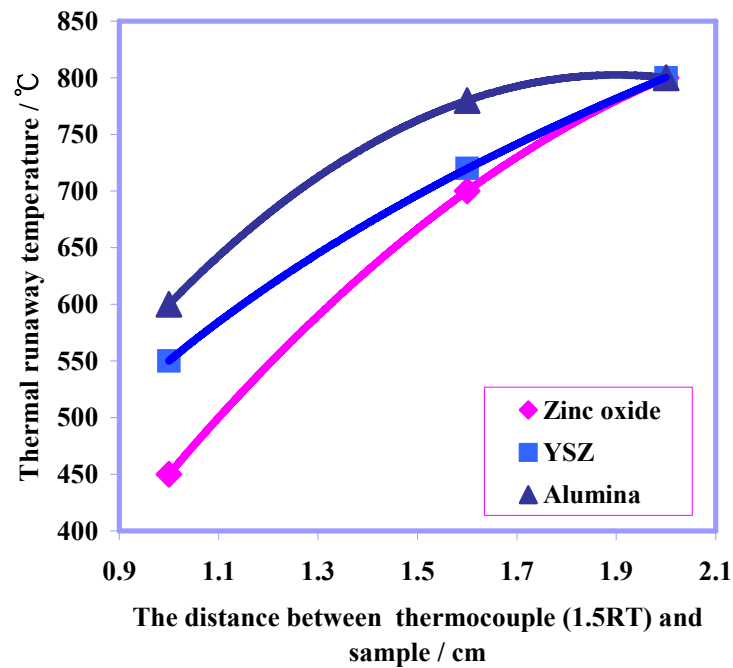


Figure 4.5. Critical temperatures causing thermal runaway for different distances between thermocouple (1.5RT) and sample for different materials.

The field-focusing effect of thermocouples was also observed by Jaglin *et. al.* during the microwave heating of a SiC-based ceramic using a thermal imaging camera, figure 4.6 [140].

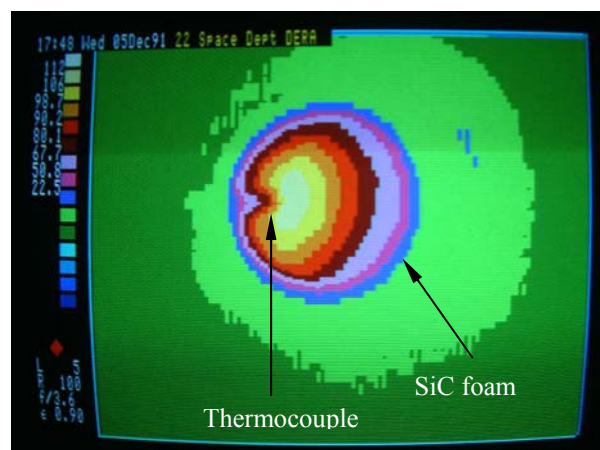


Figure 4.6. Digital thermal image of a SiC foam during microwave heating [140].

4.1.3. PROBLEMS AND IMPROVEMENT OF OFTS FOR TEMPERATURE MEASUREMENT DURING CONVENTIONAL HEATING

Table 4.2 shows the results of melting point measurement of V_2O_5 by an OFT during microwave heating and conventional heating; it can be seen that the approach is relatively accurate in both cases. However, a comparative study between a thermocouple and an OFT during conventional heating revealed that a big difference between them was observed and that the OFT always showed a higher temperature than the thermocouple when the sensors were pressed against the surfaces of a sample, figure 4.7.

Table 4.2. The melting points of V_2O_5 measured by an OFT during microwave heating and conventional heating.

Approach	Mp / °C
Microwave heating	687 ± 1
Conventional heating	685 ± 1
Measured by DSC	688.6 ± 0.5

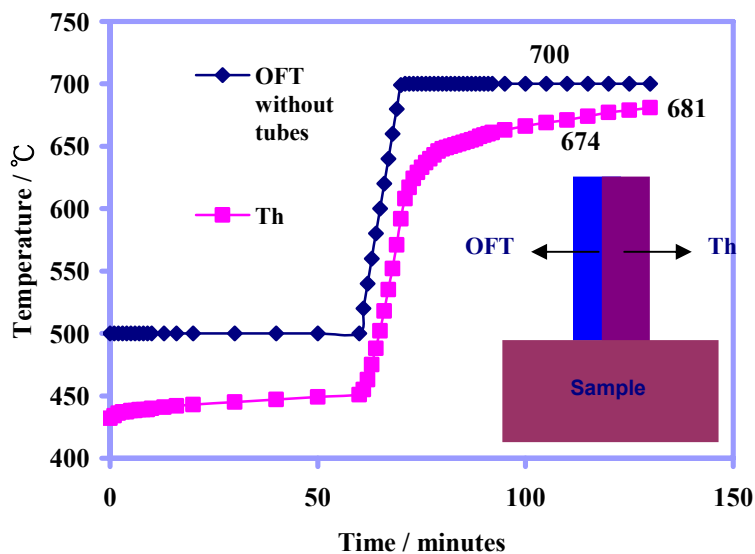


Figure 4.7. During conventional heating, when an OFT and thermocouple (Th) were pressed against the surface of a sample, the OFT was found to record a higher temperature.

It was considered that the radiation from the heating elements could affect the OFT sensor, yielding an inaccurate temperature measurement, figure 4.8.

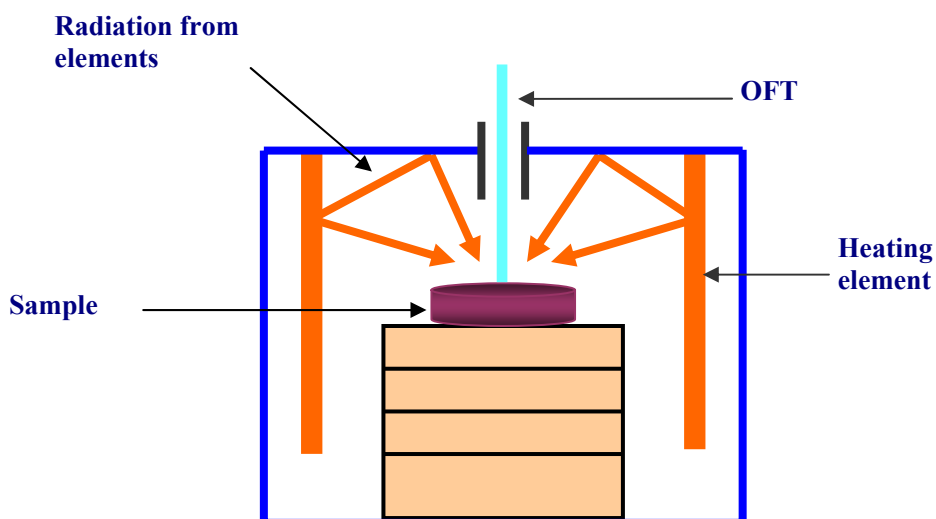


Figure 4.8. Schematic diagram of the set-up used for temperature measurement with an OFT.

When the OFT was used to measure the melting point of V_2O_5 the probe was always inserted into a powder body, suggesting that the radiation from the elements was reflected by the V_2O_5 and hence the powder centre could be regarded as a black body. The OFT was therefore not affected by the radiation during melting point measurement of the V_2O_5 powder, figure 4.9. This suggested that in order to obtain accurate temperature measurement for an OFT, the radiation from the elements needed to be shielded, figure 4.10. This will be discussed in the later sections.

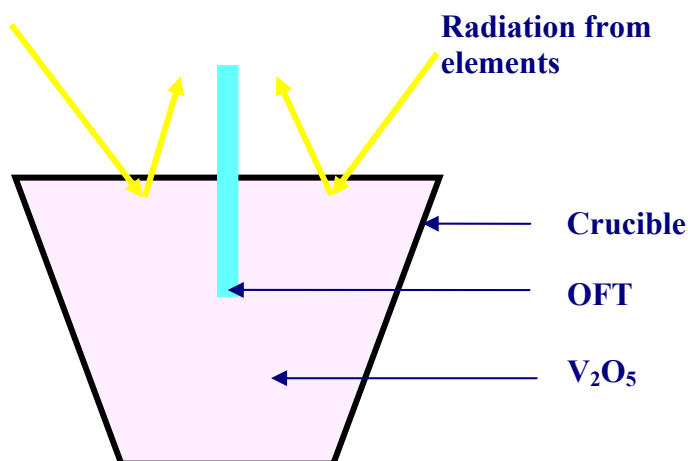


Figure 4.9. A schematic diagram of reflection of the radiation from the elements by the V_2O_5 .

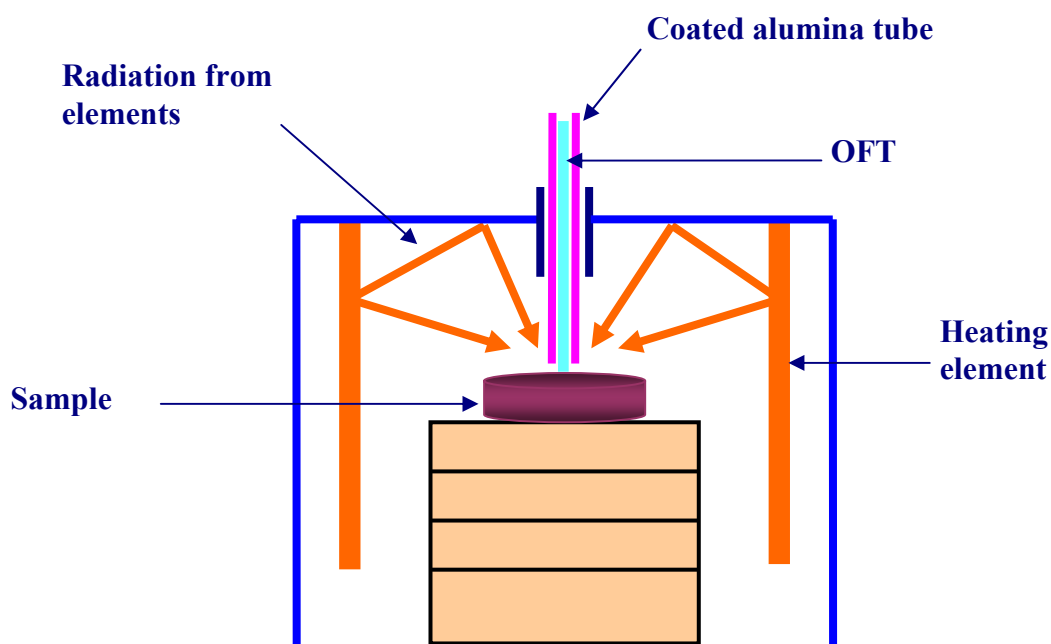
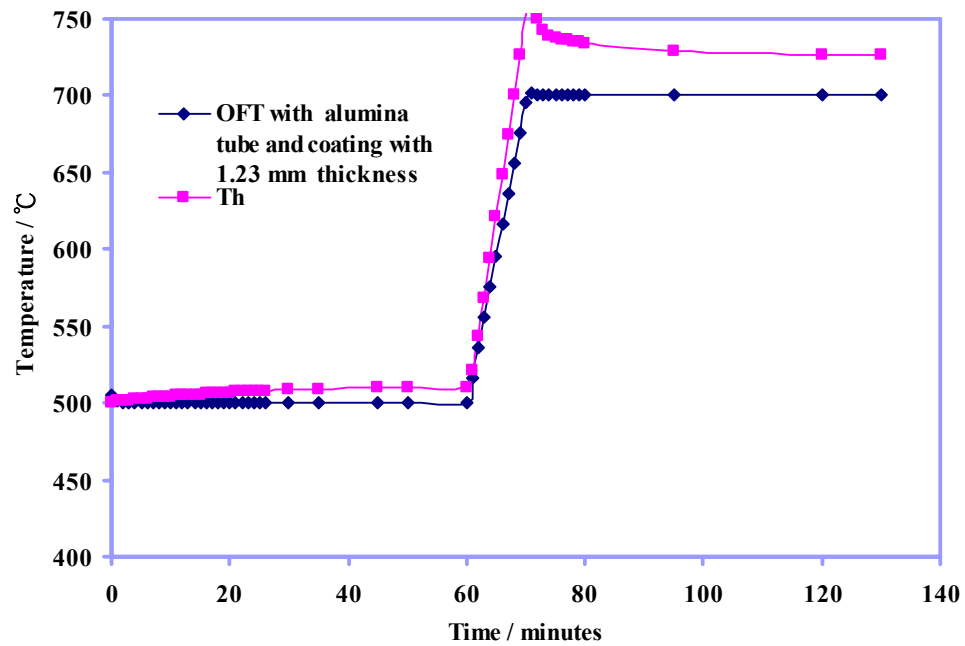
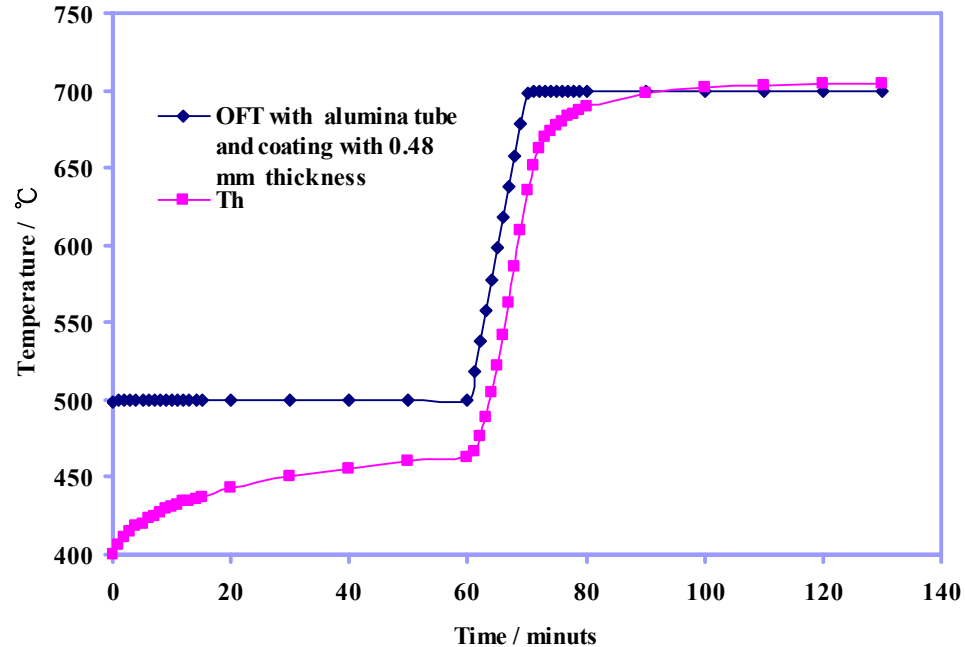


Figure 4.10. A schematic diagram of the set-up used for temperature measurement with a shielded OFT. The use of an alumina tube with a coating reduced the effect of radiation from the heating elements.

Figure 4.11 shows the effect of coating thickness on temperature measurement accuracy. The radiation energy shielded by the coating increased with the coating thickness, thus the temperature errors changed with the coating thickness.



4.11a



4.11b

Figure 4.11. The effect of thickness of a coating on temperature measurement accuracy. During the experiments, the OFT was controlled by a PID system and followed a programme set up. A temperature difference was indicated by a thermocouple (Th) arranged as shown in figure 4.7.

It should be noted that this only applied at low temperatures, table 4.3 shows that an OFT can measure temperature reasonably accurately at high temperatures during conventional heating.

Table 4.3. The comparison of temperature measurement between an OFT and a type S thermocouple which has been calculated by the melting point measurement of V_2O_5 and CuO_2 at high temperature during conventional heating.

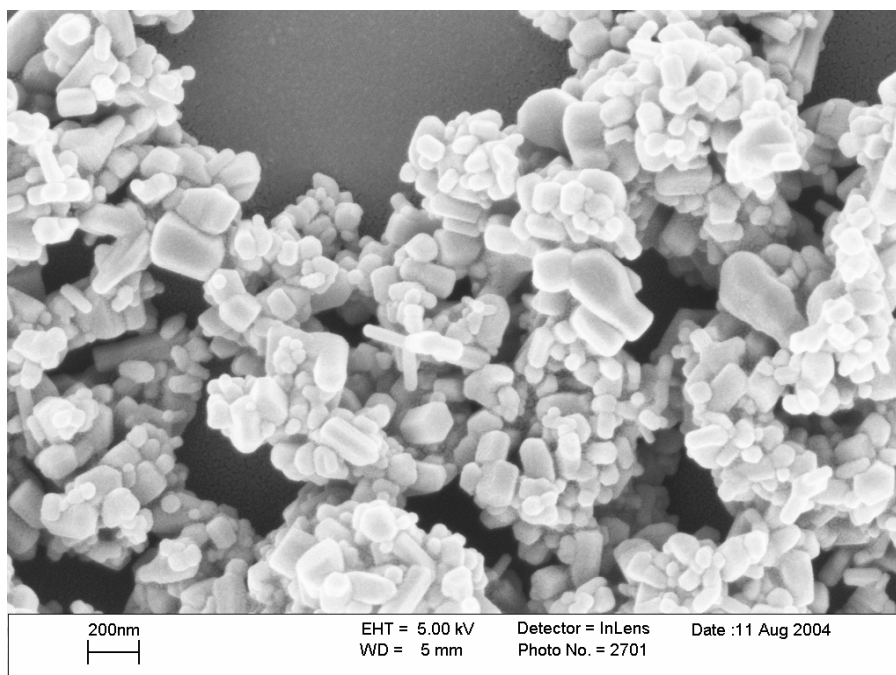
Measured temperature / °C,	
Optical fibre thermometer	Type S thermocouple
950 ± 2	938 ± 1
1000 ± 1	992 ± 1
1050 ± 1	1048 ± 2
1100 ± 1	1101 ± 2
1200 ± 1	1205 ± 3

4.2. SINTERING EXPERIMENTS

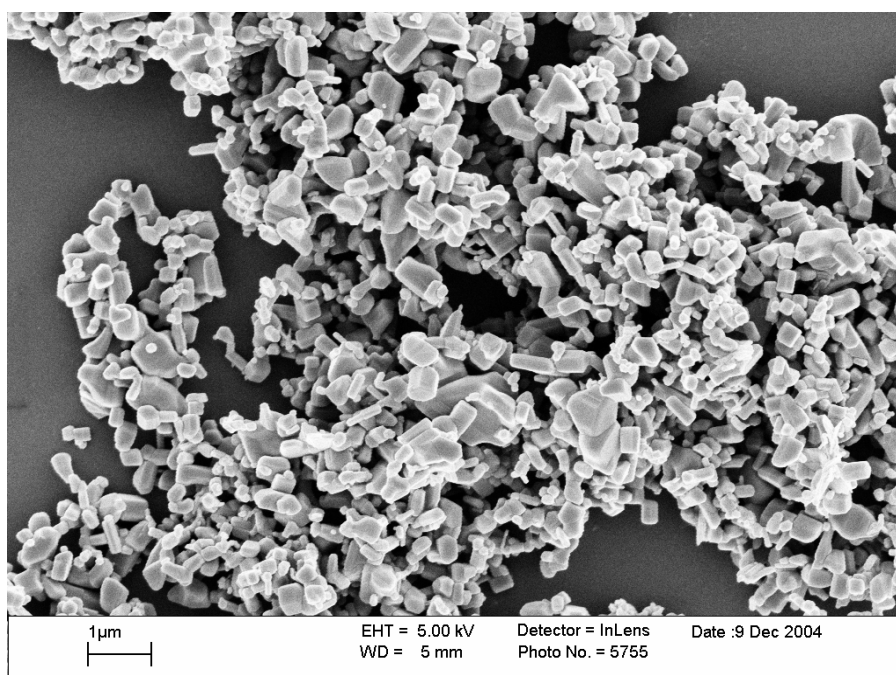
4.2.1. SINTERING

4.2.1.1. *FEG-SEM OBSERVATION OF POWDERS*

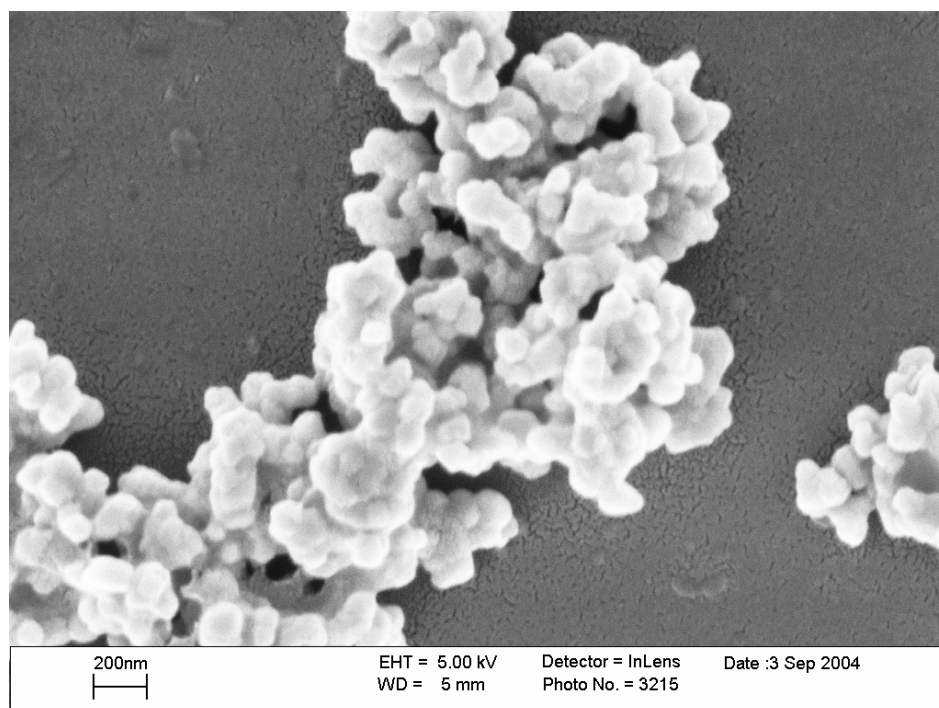
Figure 4.12 shows the micrographs of powders before being pressed into pellets. The grain size distribution is from a few nano meters to a few microns.



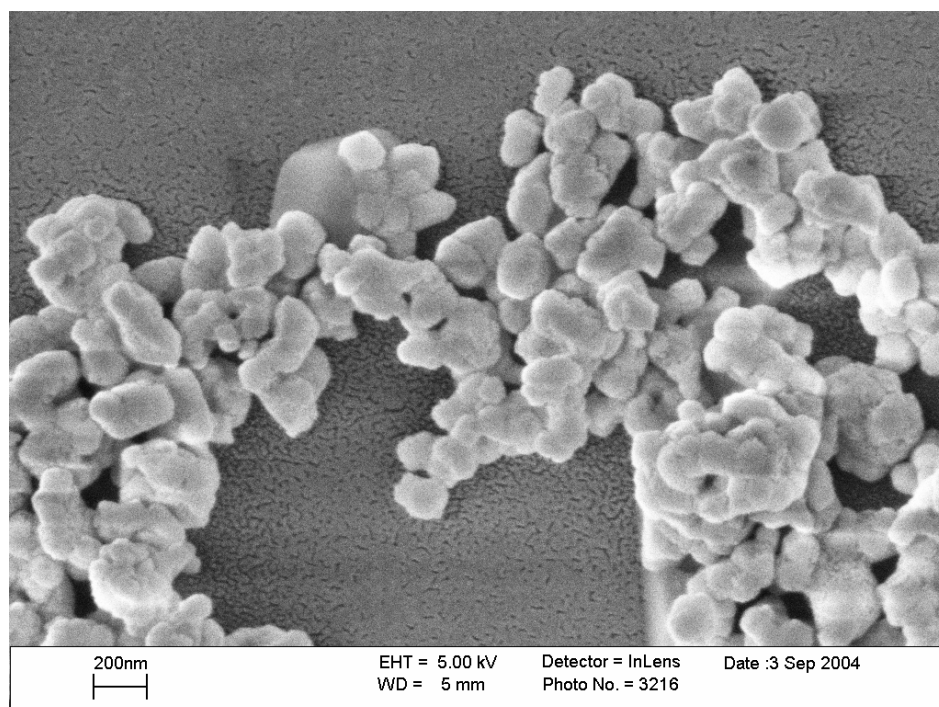
a: submicron powder of ZnO (Sigma-Aldrich)



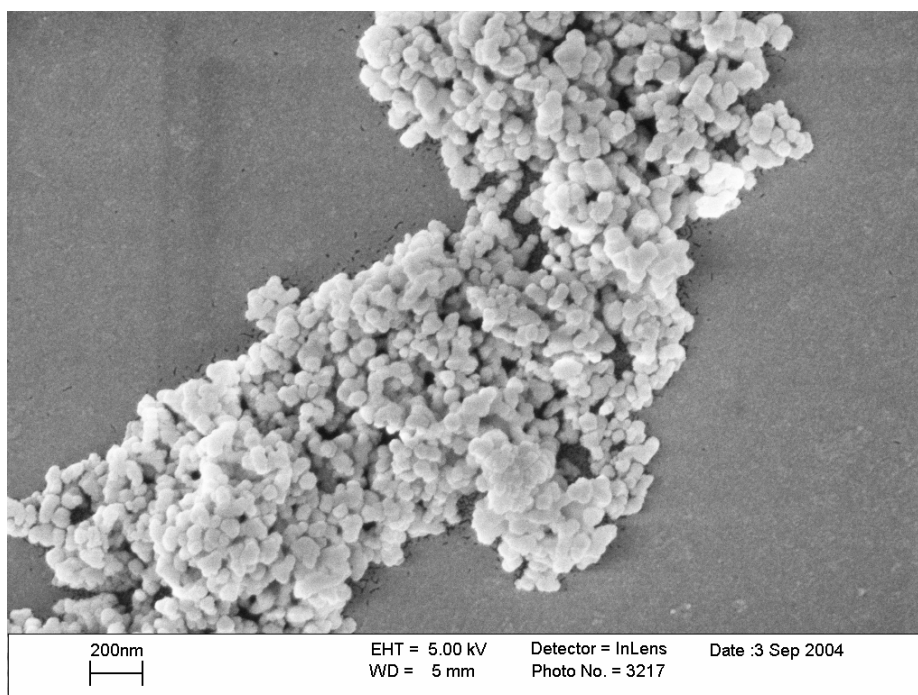
b: micron powder of ZnO (Sigma-Aldrich)



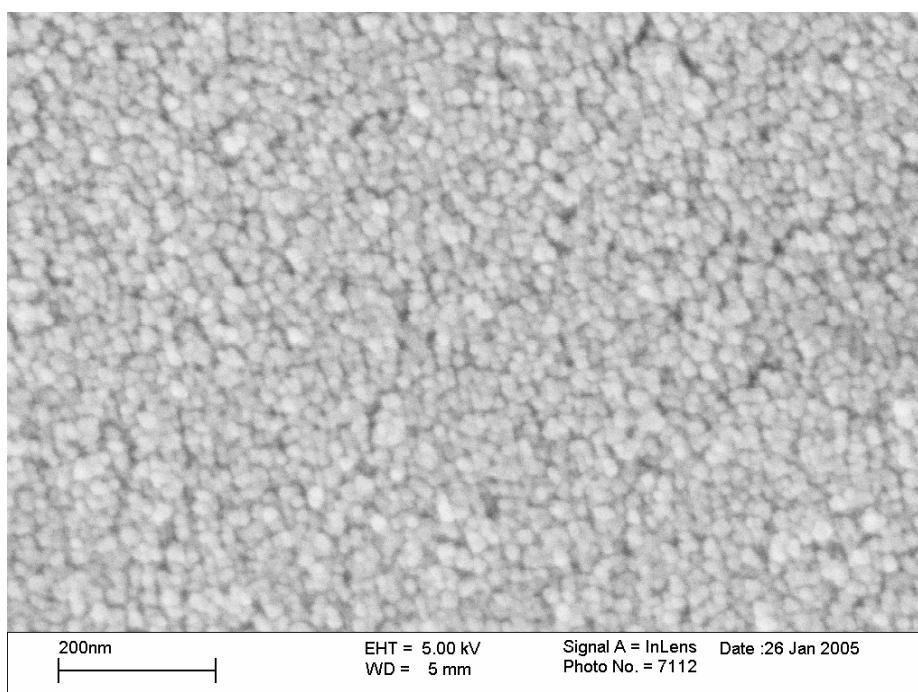
c: submicron powder of 3-YSZ (MEL)



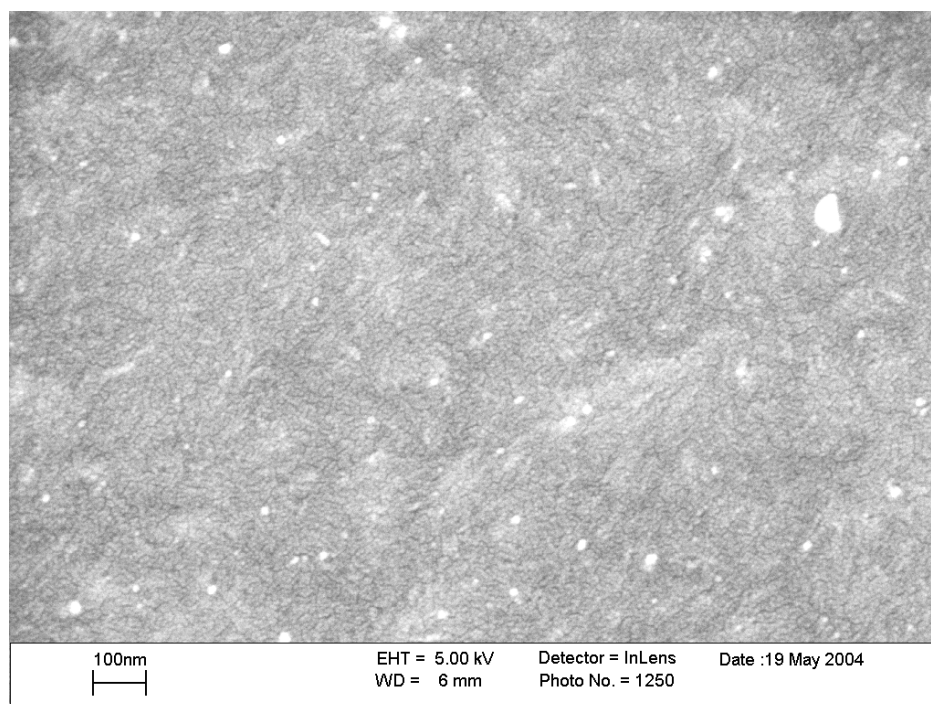
d: submicron powder of 10-YSZ (MEL)



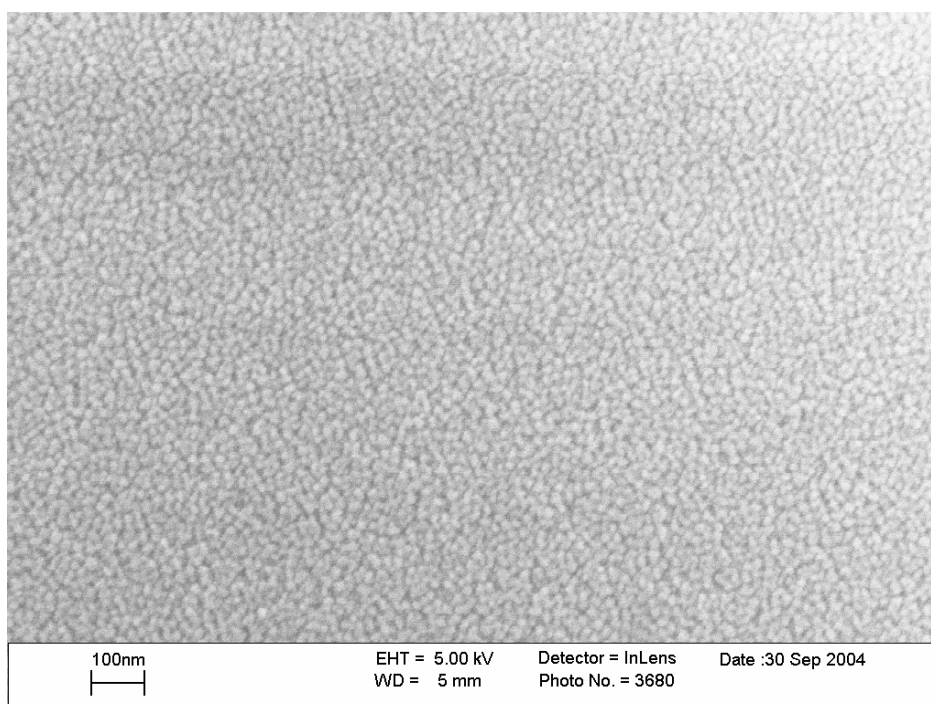
e: submicron powder of 3-YSZ (HSY-3U)



f: nano powder of 3-YSZ (MEL)



g: Sol-gel alumina after calcining at 500°C



h: nano powder of silica (Sigma-Aldrich)

Figure 4.12. FEG-SEM micrographs of zinc oxide, YSZ, alumina and silica powder.

4.2.1.2. THE SELECTION OF SINTERING TEMPERATURES

Figure 4.13 shows the density curve for submicron ZnO sintered by pure conventional power as a function of temperature. It can be seen that at any temperature between 600°C and 800°C, the relative density of ZnO sintered in conventional heating will not be greater than 90%, hence, it can be used as the sintering temperature to investigate the microwave effect. Similar methods have been used in the selection of sintering temperature for other materials.

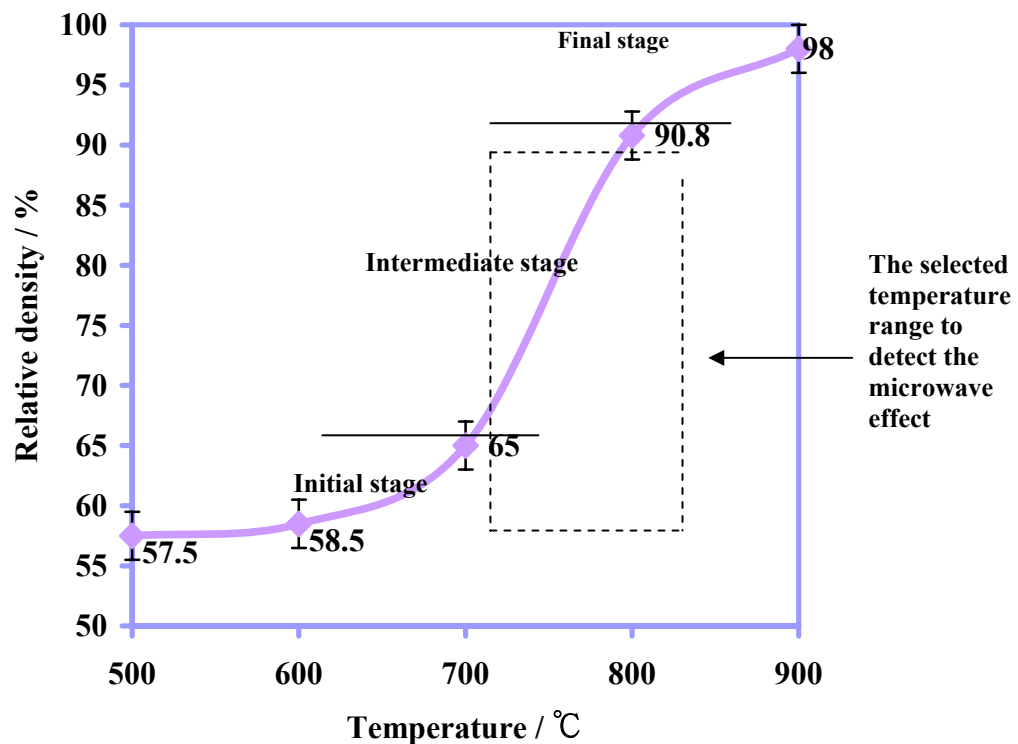
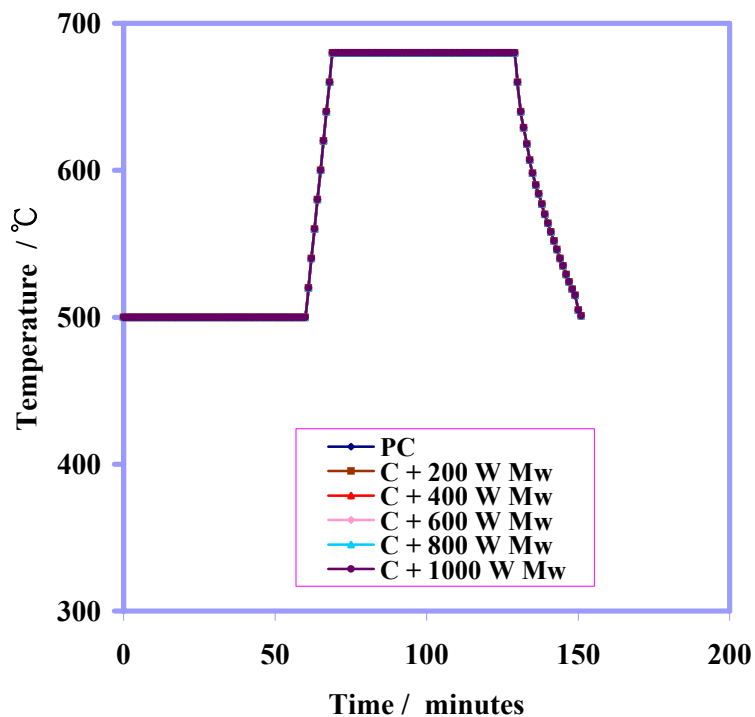


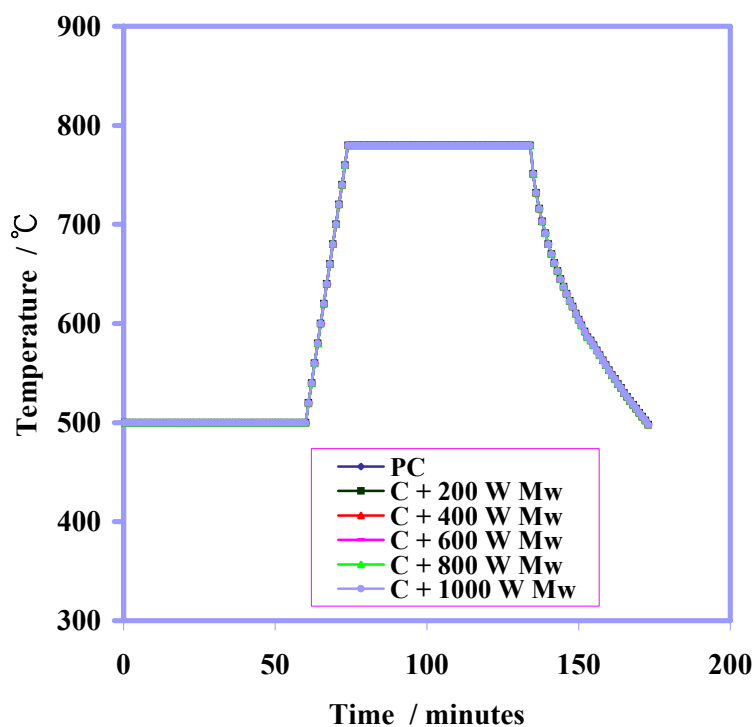
Figure 4.13. Densities of submicron ZnO sintered for one hour by pure conventional power as a function of temperature.

4.2.1.3. TEMPERATURE - TIME PROFILE

Figures 4.14 and 4.15 show the temperature – time curves for ZnO samples sintered at 680°C, 780°C and 900°C for one hour. It can be seen that all the samples underwent identical temperature – time profiles irrespective of the amount of microwave power used. Similar curves were obtained for the 3-YSZ samples sintered at 1100°C and 1200°C, figure 4.16.

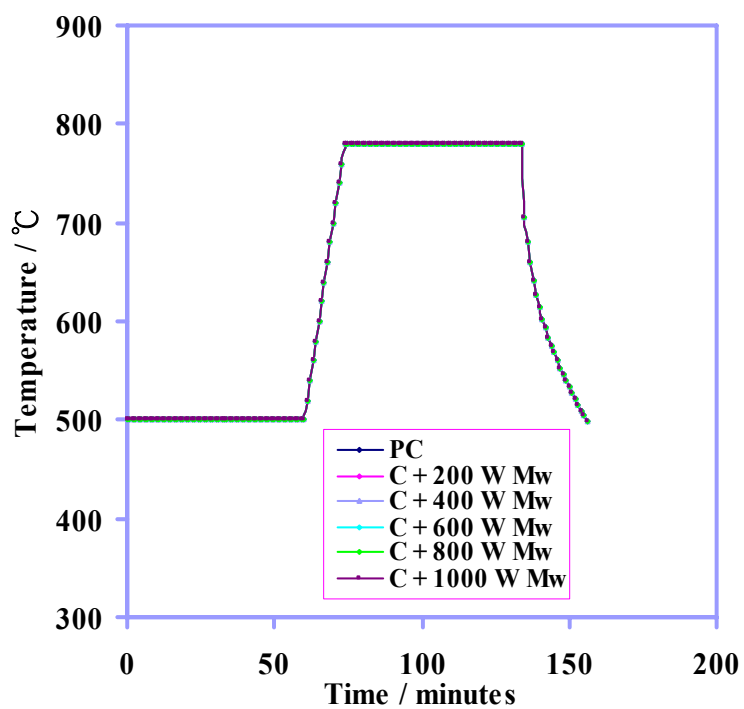


a

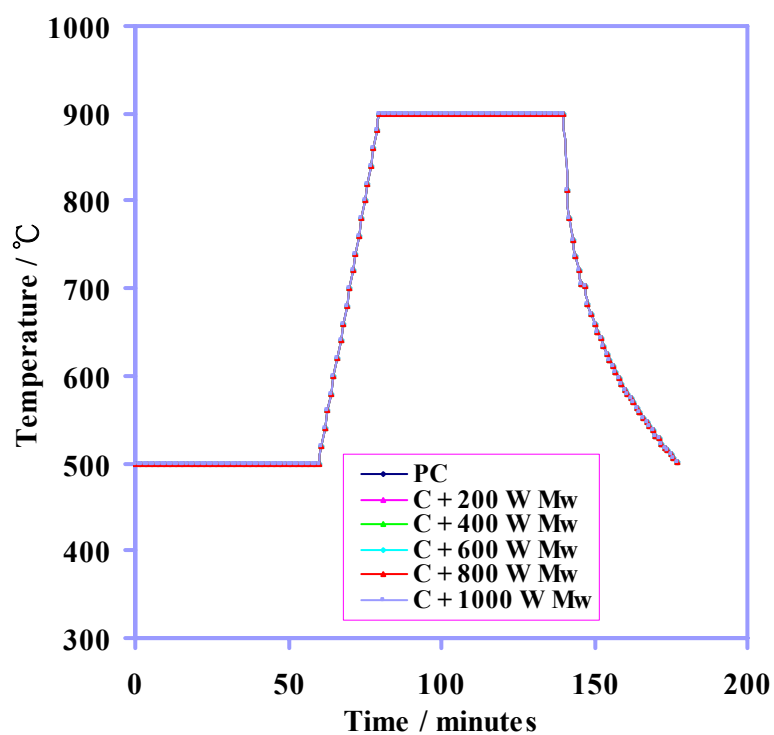


b

Figure 4.14. Sintering curves of submicron ZnO at (a) 680 °C and (b) 780 °C using hybrid heating with different microwave power(0, 200 W, 400W, 600 W, 800 W and 1000 W) – all the curves are identical (central temperature control).

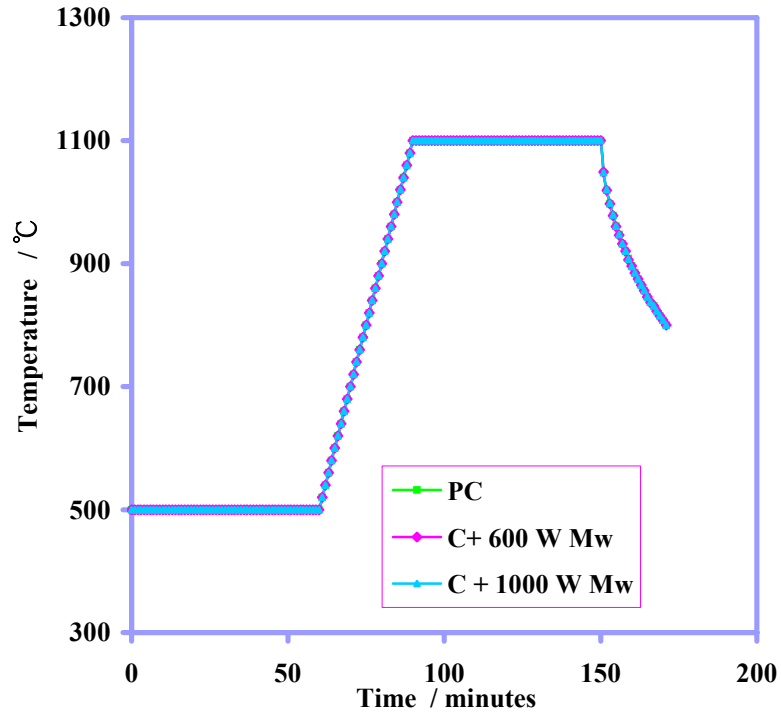


a

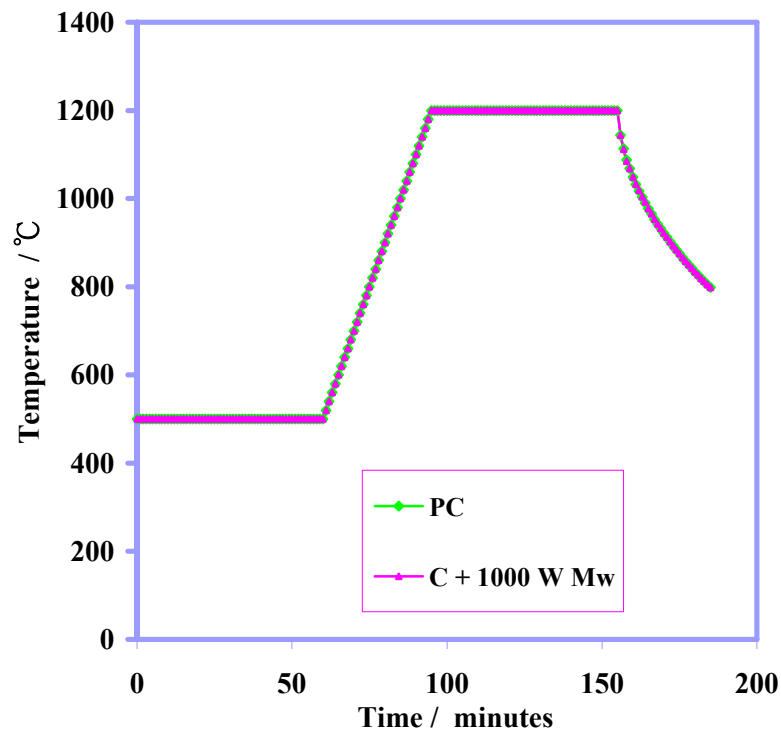


b

Figure 4.15. Sintering curves of ZnO at (a) 780 °C and (b) 900 °C using hybrid heating with different microwave power (0, 200 W, 400 W, 600 W, 800 W and 1000 W) – all the curves are identical (surface temperature control).



a



b

Figure 4.16. Sintering curves of YSZ at (a) 1100 °C and (b) 1200 °C using hybrid heating with different microwave power (0, 600 W and 1000 W) – all the curves are identical (surface temperature control).

Figures 4.17 and 4.18 shows the level of conventional power needed to achieve the temperature–time profile in the sintering of ZnO shown in figures 4.14 and 4.15 as a function of the different levels of microwave power used. Similar sintering and conventional power application curves were also used for sintering 3-YSZ, as shown in figure 4.19, as well as other samples such as 10-YSZ, alumina and silica.

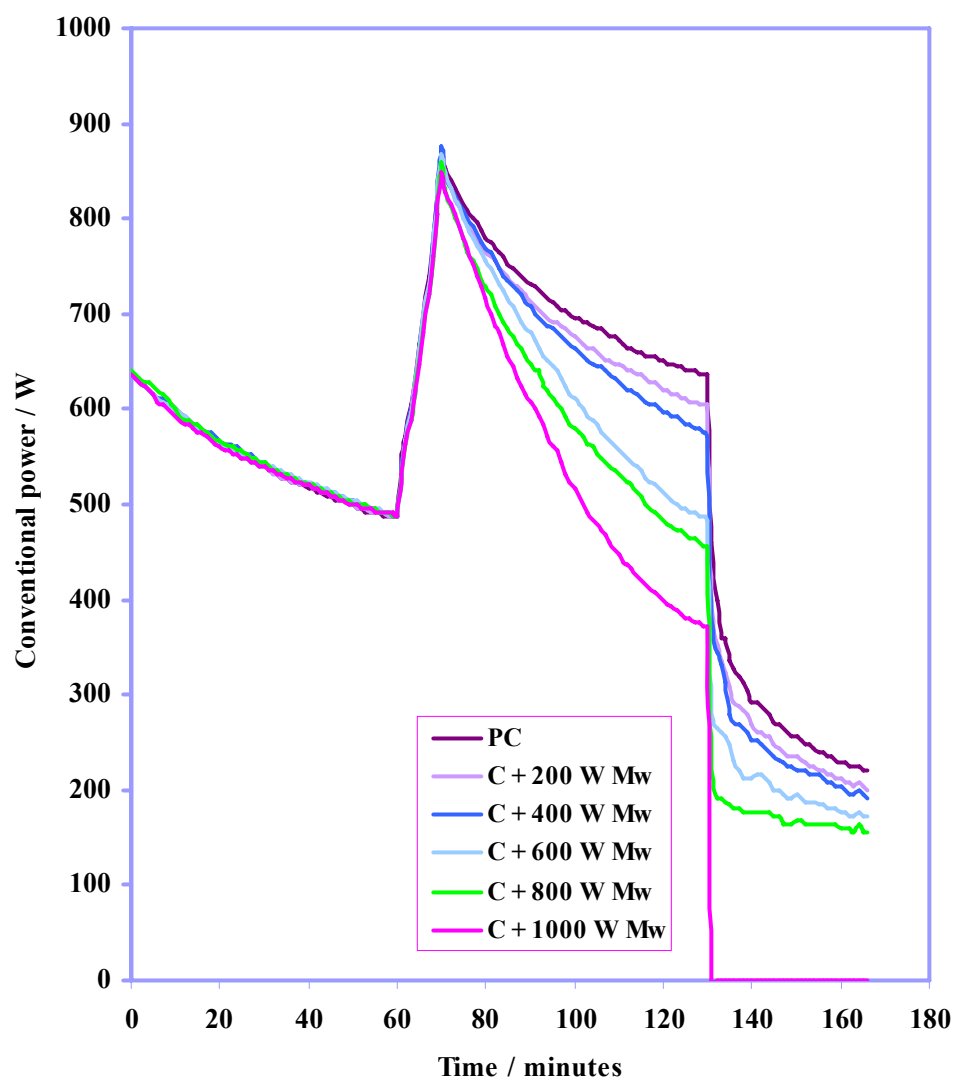


Figure 4.17. Conventional power control during sintering of ZnO at 680 °C during hybrid heating with different microwave power(0, 200 W, 400W, 600 W, 800 W and 1000 W) (central temperature control).

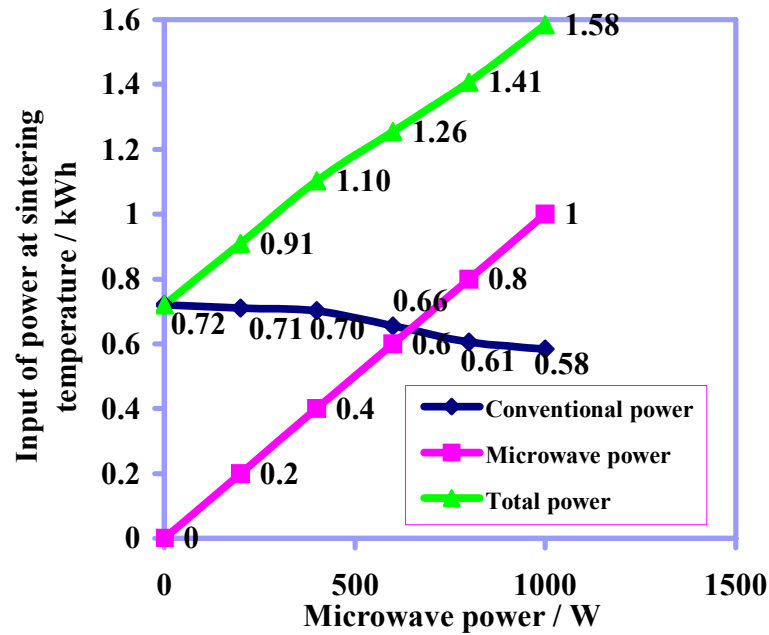


Figure 4.18. Input of power in 1 hour at sintering temperature (680 °C) for different hybrid sintering with different microwave power (0, 200 W, 400 W, 600 W, 800 W and 1000 W) of submicron ZnO.

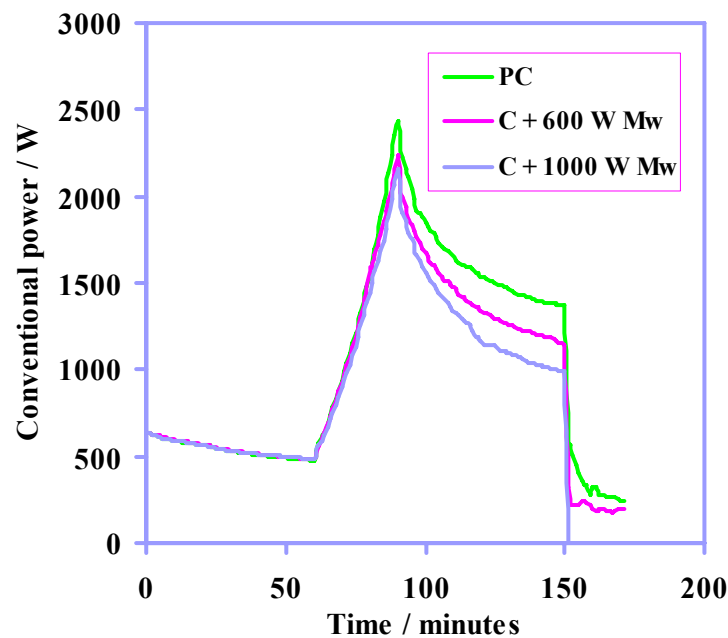


Figure 4.19. Power control during sintering of YSZ at 1100 °C using hybrid heating with different microwave power (0, 600 W, and 1000 W) (surface temperature control).

4.2.1.4. DENSIFICATION

4.2.1.4.1. Zinc Oxide

Figure 4.20 and 4.21 illustrate the influence of the amount of microwave power on the resulting density of the pellets from the submicron- and micron-sized ZnO powders after sintering at 680°C, 780°C, and 900°C respectively. A maximum of a >20% increase in density was gained in the submicron and micron ZnO samples respectively at 680°C and 780°C in hybrid heating compared to that in conventional heating.

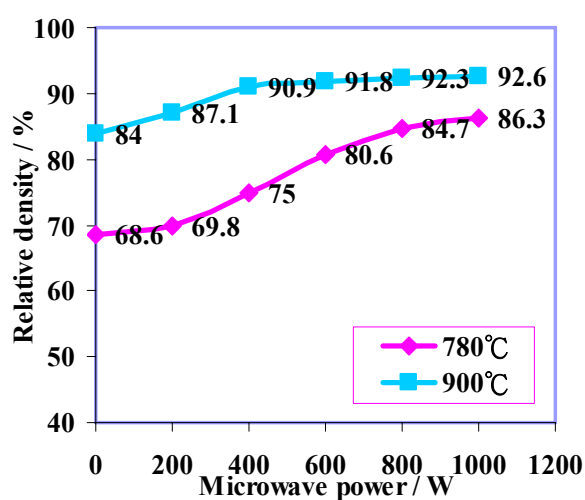


Figure 4.20a. Density curves of micron ZnO hybrid sintered at 780 °C and 900 °C (surface temperature control).

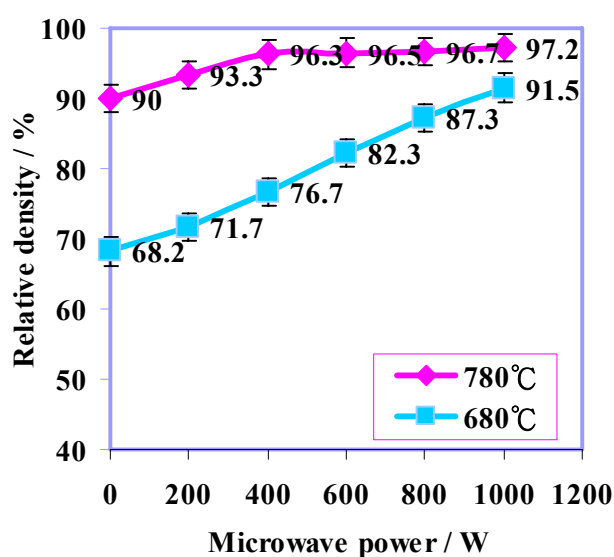


Figure 4.20b. Density curves of submicron ZnO hybrid sintered at 680 °C and 780 °C (surface temperature control).

The identical density curves were obtained in all the small samples with different sizes during hybrid heating under the same sintering conditions as shown in figure 4.21a. However, a big increase in density was observed in the large sample as shown in figure 4.21b.

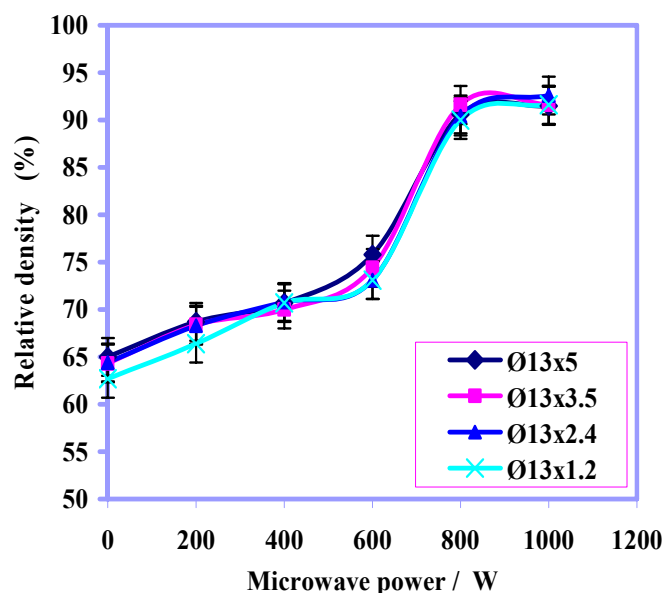


Figure 4.21a. Density curves of submicron ZnO pellets with different sizes ($\Phi 13 \times 5$, $\Phi 13 \times 3.5$, $\Phi 13 \times 2.4$ and $\Phi 13 \times 1.2$) and hybrid sintered at $680\text{ }^{\circ}\text{C}$ (central temperature control).

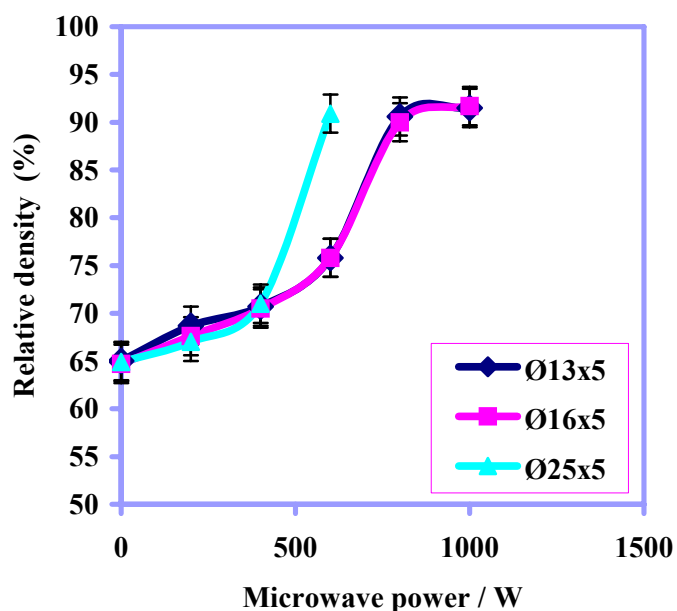


Figure 4.21b. Density curves of submicron ZnO pellets with different sizes ($\Phi 13 \times 5$, $\Phi 16 \times 5$ and $\Phi 25 \times 5$) hybrid sintered at $680\text{ }^{\circ}\text{C}$ (central temperature control).

The enhanced densification in hybrid heating appeared to be more dominant in the intermediate stage of sintering as shown in figure 4.22.

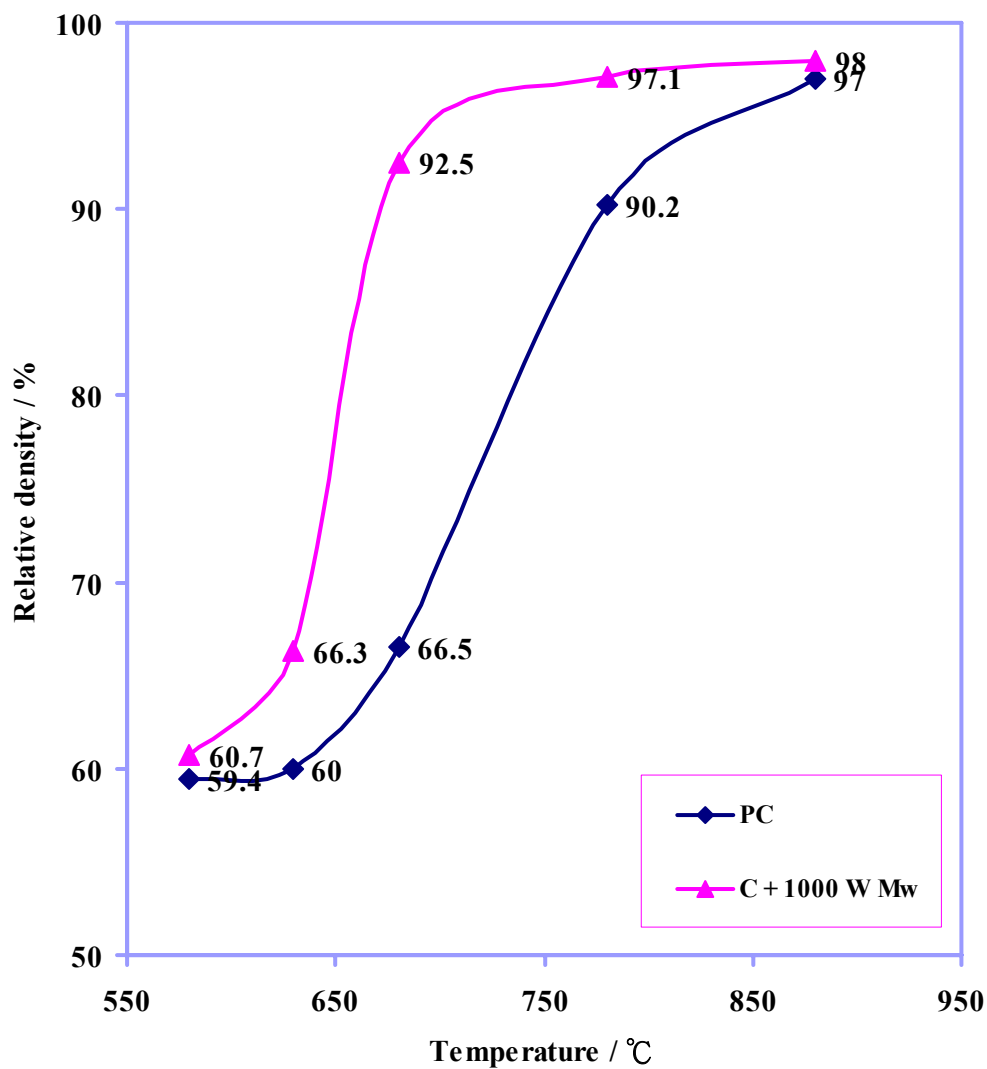
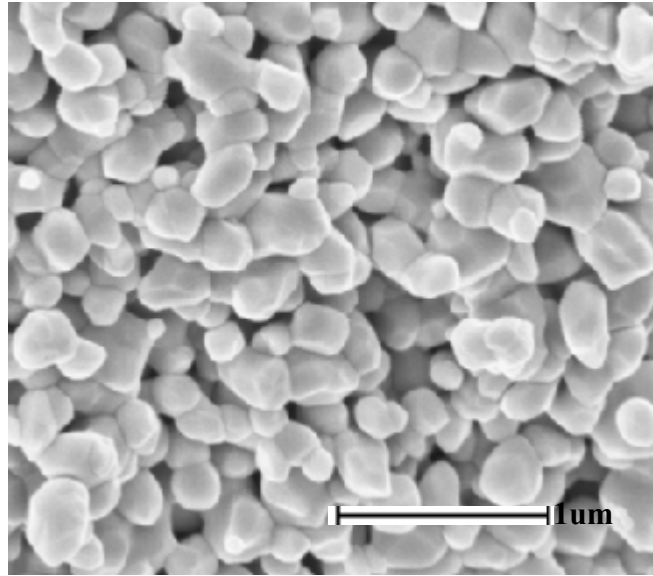
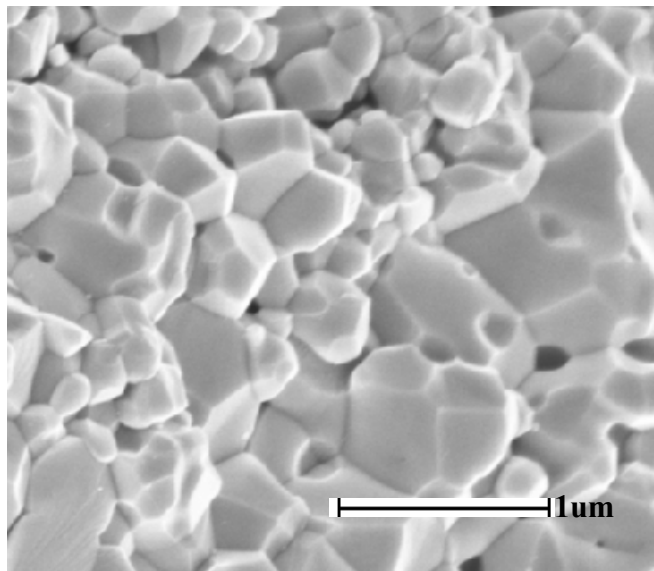


Figure 4.22. Density curves of submicron ZnO sintered at different temperatures during pure conventional heating and hybrid heating with 1000 W microwave power.

Figures 4.23, 4.24 and 4.25 show the microstructures of the pellets from the ZnO powders after sintering at 680°C (submicron) and 780°C (micron) using pure conventional power and hybrid heating involving 1000W of microwave power. Higher density and bigger grains indicate the enhancement of densification in hybrid heating.

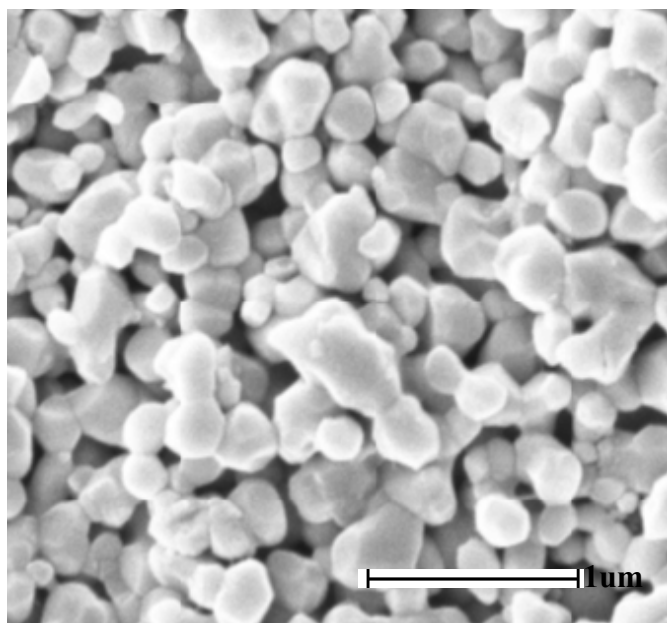


4.23 (a)

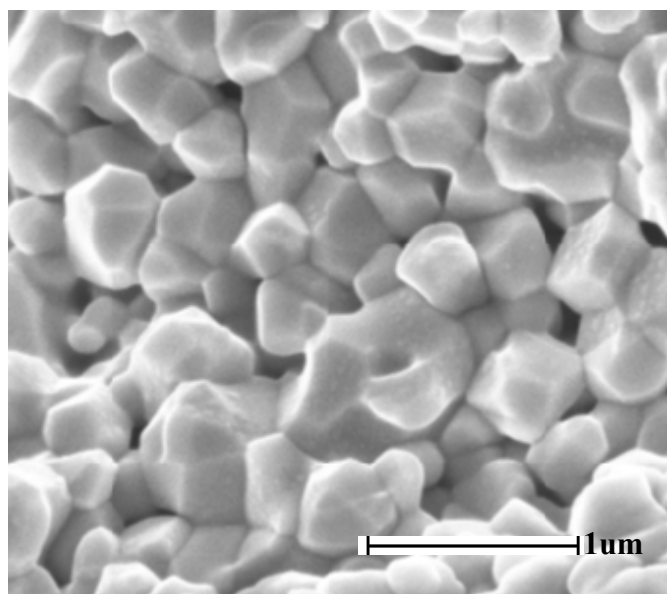


4.23 (b)

Figure 4.23. FEG-SEM micrographs of fracture surfaces of submicron ZnO sintered at 680 °C (surface temperature control) using (a) conventional heating and (b) hybrid heating with 1000 W microwave power.

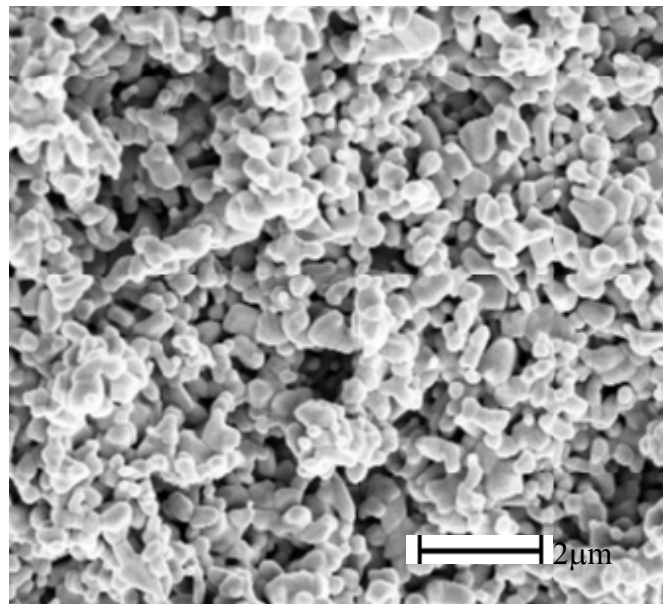


4.24 (a)

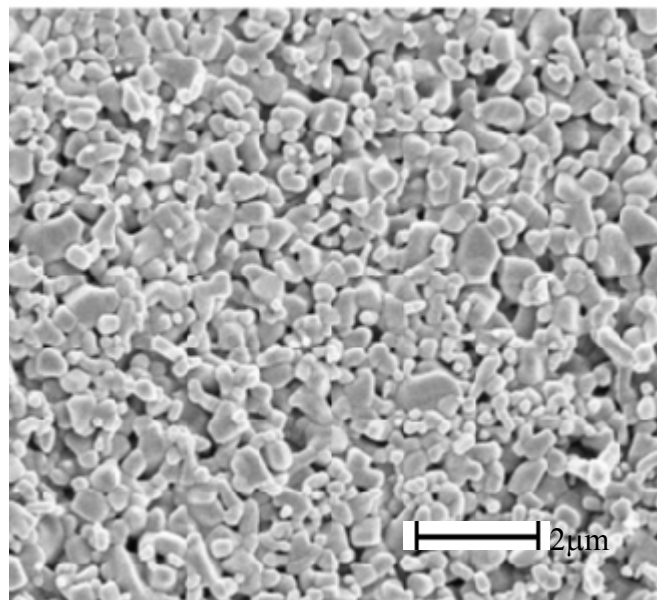


4.24 (b)

Figure 4.24. FEG-SEM micrographs of fracture surfaces of submicron ZnO sintered at 680 °C (central temperature control) using (a) conventional heating and (b) hybrid heating with 1000 W microwave power.



4.25 a



4.25 b

Figure 4.25. FEGSEM micrographs of fracture surfaces of micron ZnO sintered at 780 °C using (a) conventional heating and (b) hybrid heating with 1000 W microwave power (surface temperature control).

4.2.1.4.2. YSZ

The enhanced densification was also observed in hybrid sintering of submicron-sized 3-YSZ (HSY-3U) and nano-sized 3-YSZ (MEL) powders as shown in figures 4.26 and 4.27.

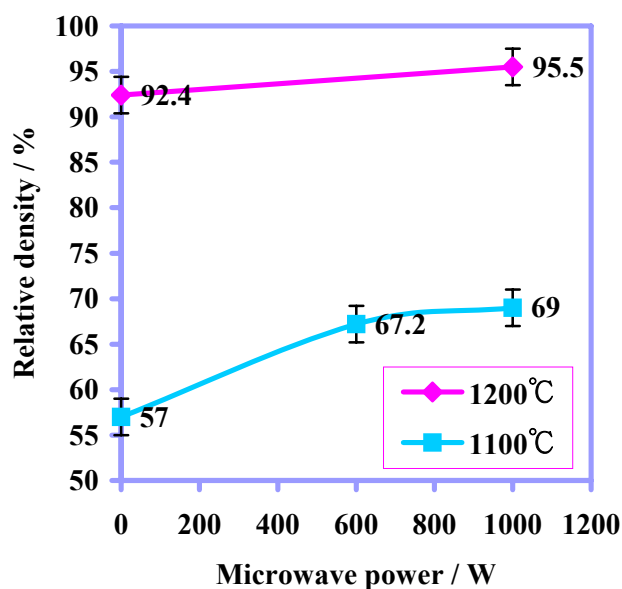


Figure 4.26. Density curves of submicron YSZ hybrid sintered at 1100 °C and 1200 °C (surface temperature control).

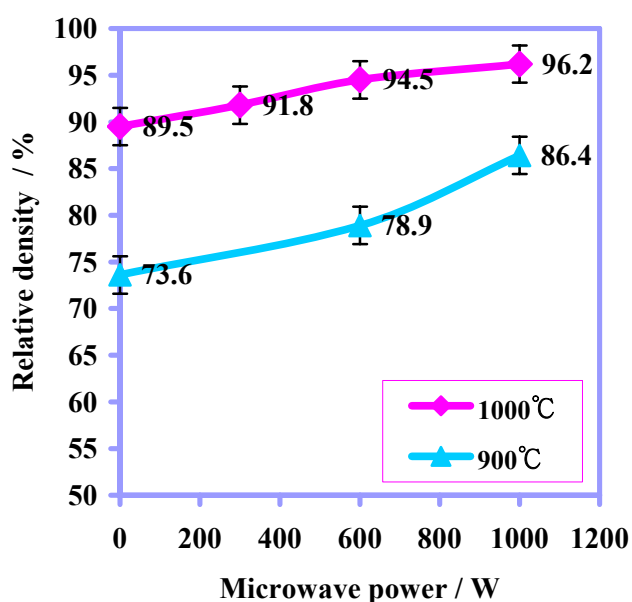
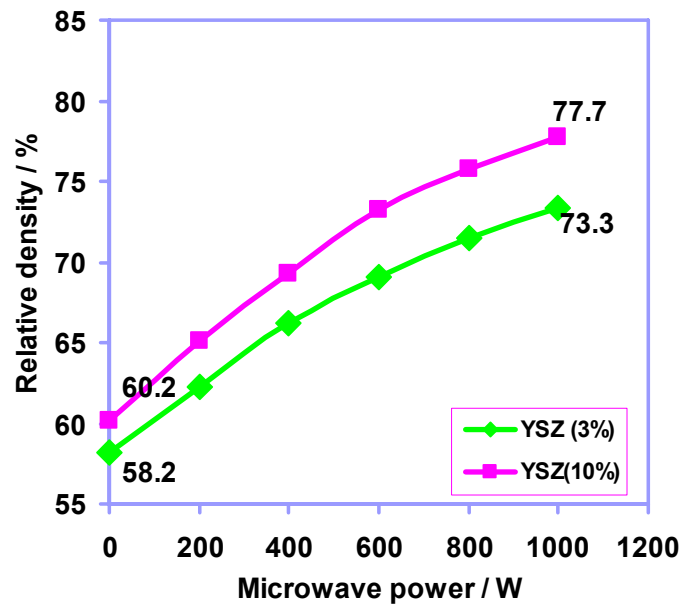
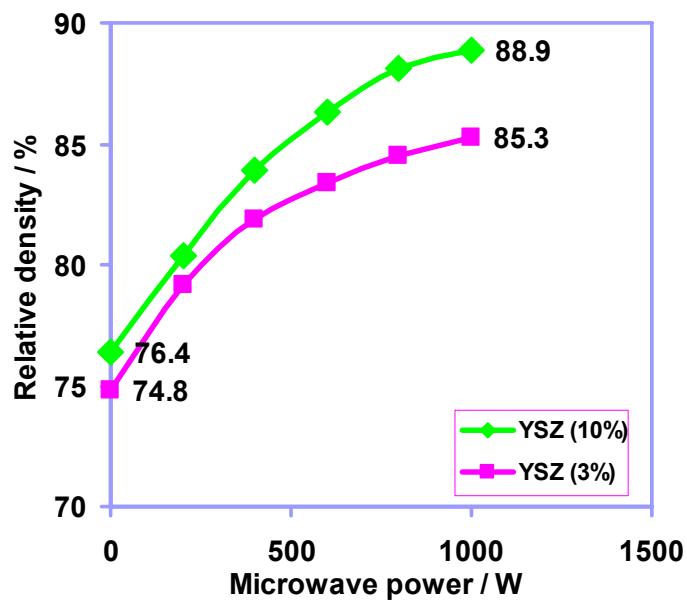


Figure 4.27. Density curves of nano YSZ sintered at 900 °C and 1000 °C (Surface temperature control).

Figure 4.28 shows that the enhanced densification were obtained during the hybrid sintering of both submicron-sized 3-YSZ and 10-YSZ (MEL).



a



b

Figure 4.28. Density curves of submicron 3-YSZ and 10-YSZ hybrid sintered at (a) 1220 °C and (b) 1260 °C (central temperature control).

Microstructural examination revealed that a higher density was achieved in the 3-YSZ pellets sintered with hybrid heating compared to that in conventional heating, figure 4.29.

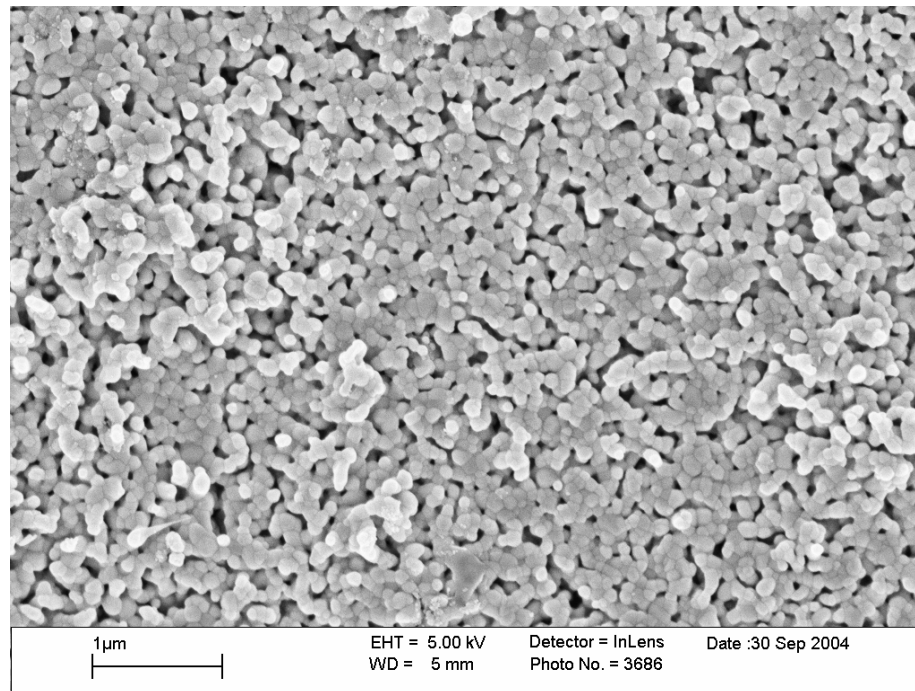
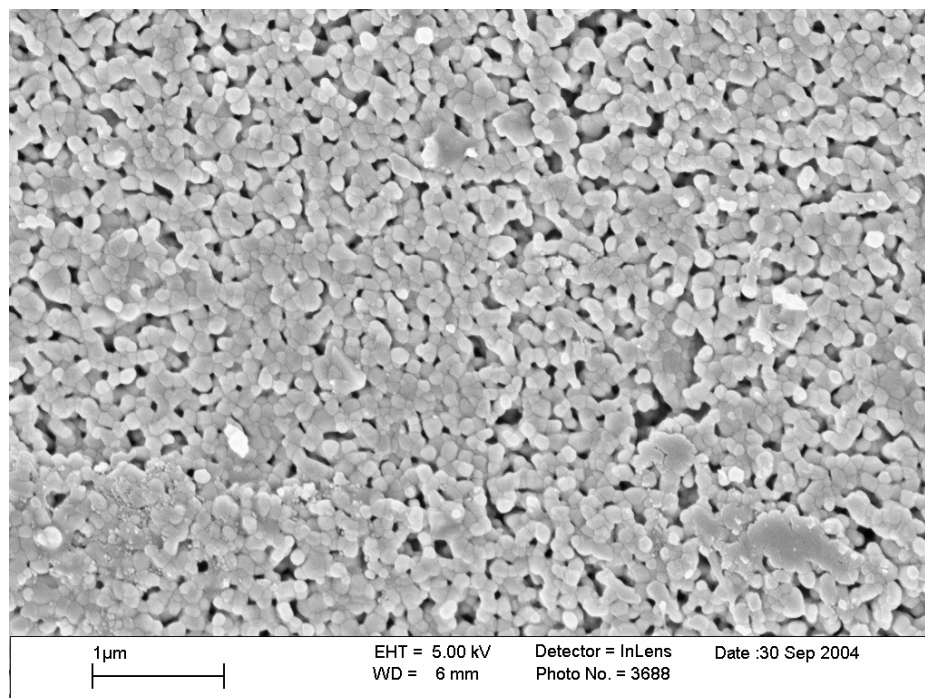
**a****b**

Figure 4.29. FEG-SEM micrographs of submicron 3-YSZ sintered at 1100 °C using (a) conventional heating and (b) hybrid heating with 1000 W microwave power (central temperature control).

4.2.1.4.3. Alumina

(1) Pellets

Tables 4.4 and 4.5 show the densities of the nano alumina pellets sintered in pure conventional and hybrid heating, the increase in density was considerably smaller than in either ZnO or YSZ and at the limit of experimental error.

Table 4.4. Relative densities of commercial nano alumina pellets (Ø13×5) sintered at 1400 °C.

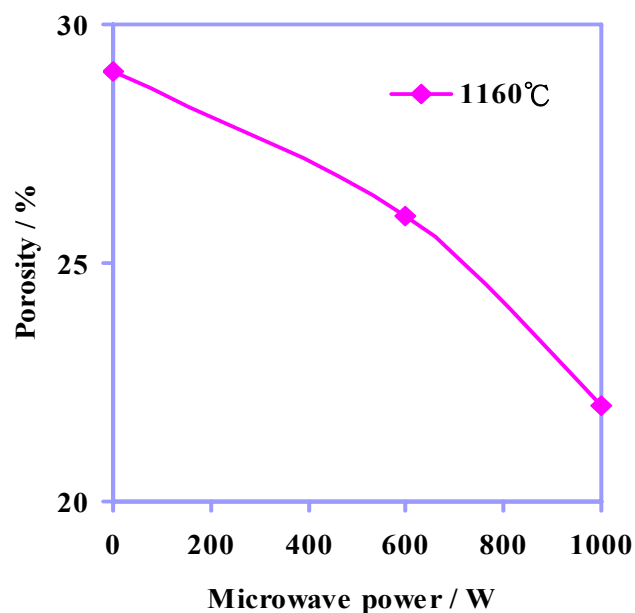
Approach	Relative density / %
PC	84
C+ 1000 W	85
Green body	50

Table 4.5. Relative densities of sol-gel synthesised nano alumina pellets (Ø13×5) sintered at 1180 °C and 1260 °C.

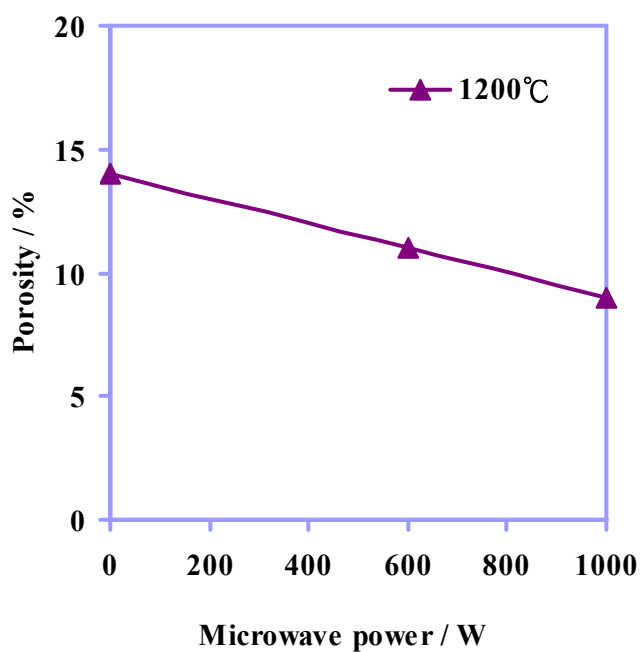
Approach	Relative density %	
	1260°C	1180°C
PC	61	57
C + 1000 W	62	59
Green body	35	

(2) Films

Sol-gel derived alumina films with a green density of about 50% were sintered using the same method as the alumina pellets. Interestingly, an enhancement in densification was observed with hybrid heating as shown in figures 4.30 and 4.31.

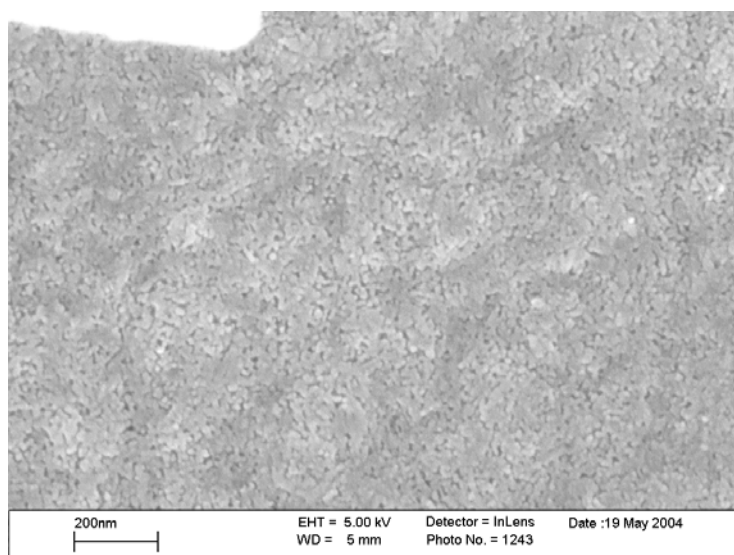


a

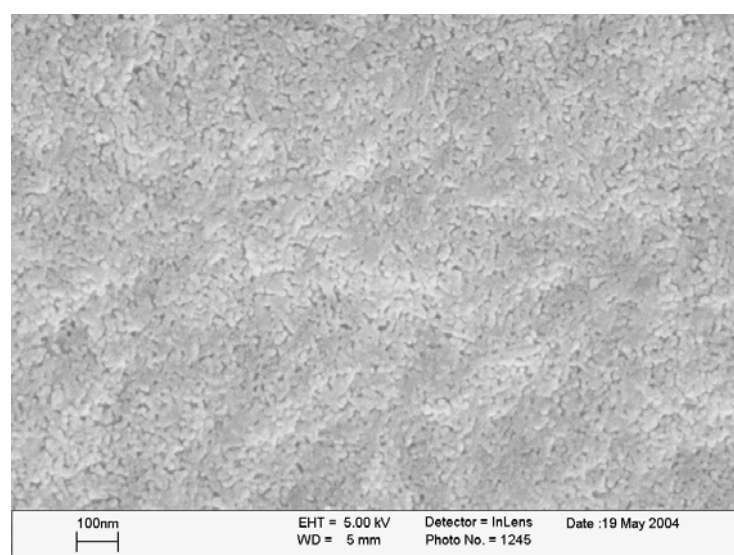


b

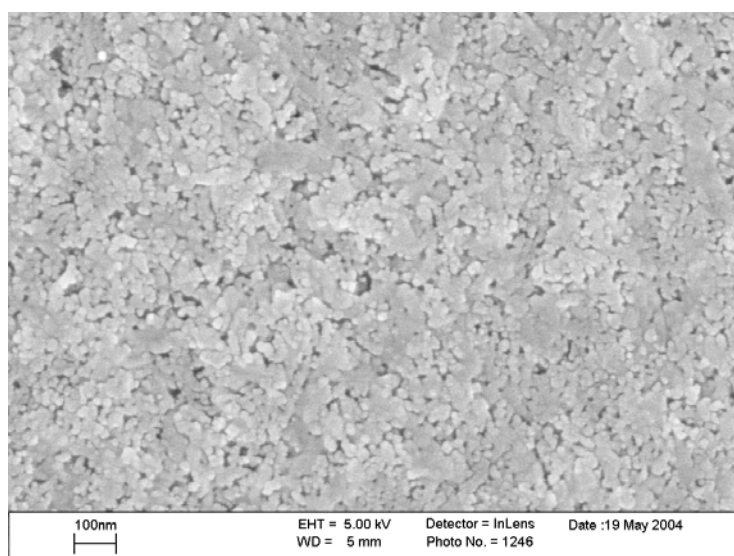
Figure 4.30. Porosity curves of annealed alumina films at 1160 °C and 1200 °C.



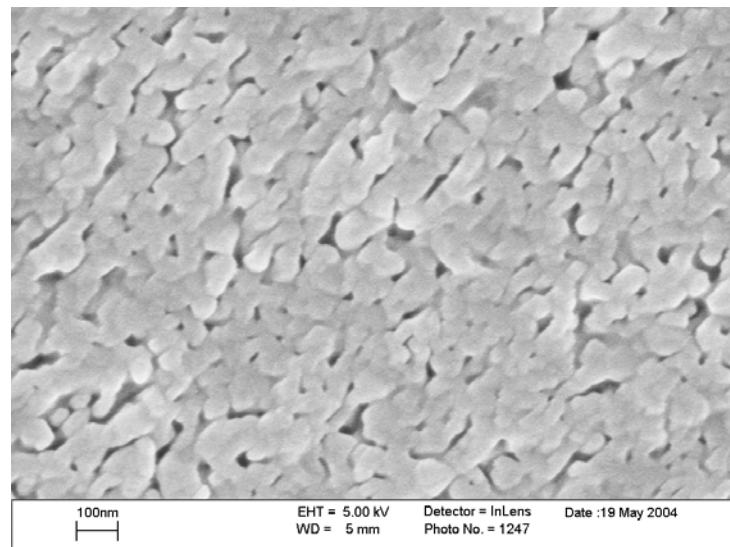
a: pure conventional heating, 1160 °C



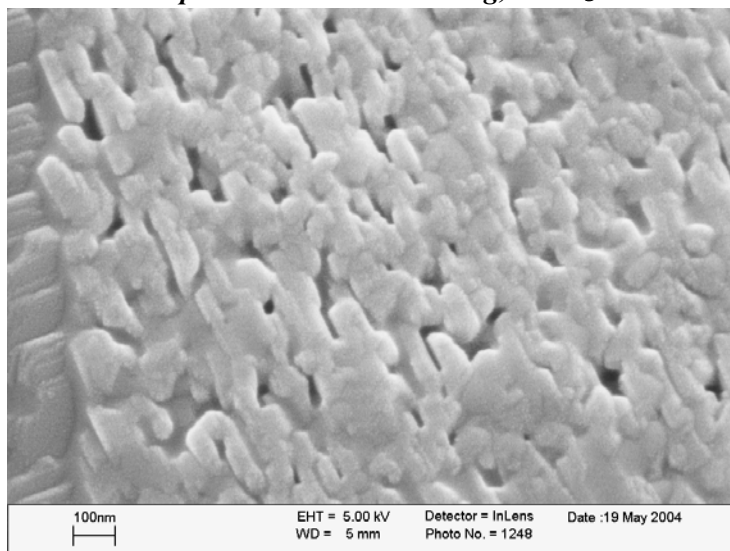
b: hybrid heating with 600 W microwave power, 1160 °C



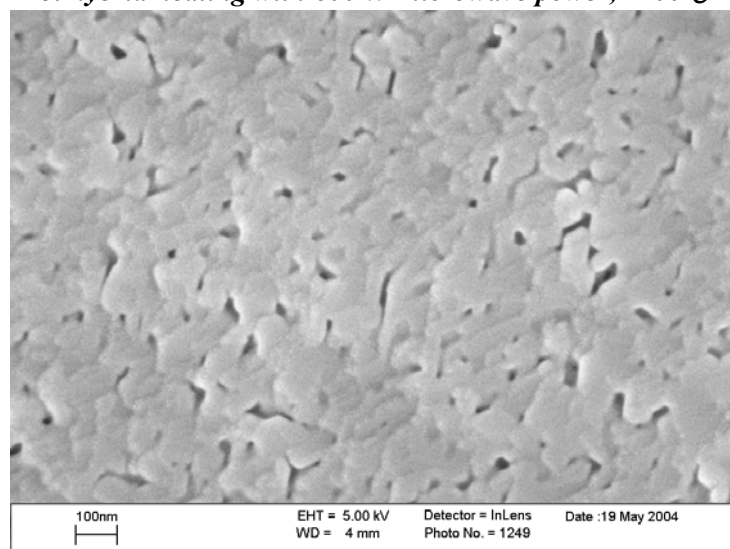
c: hybrid heating with 1000 W microwave power, 1160 °C



d: pure conventional heating, 1200 °C



e: hybrid heating with 600 W microwave power, 1200 °C



f: hybrid heating with 1000 W microwave power, 1200 °C

Figure 4.31. FEG-SEM micrographs of sol gel alumina films after annealing.

Figure 4.32 show that sol-gel alumina films before annealing and after annealing were γ and α phase, respectively.

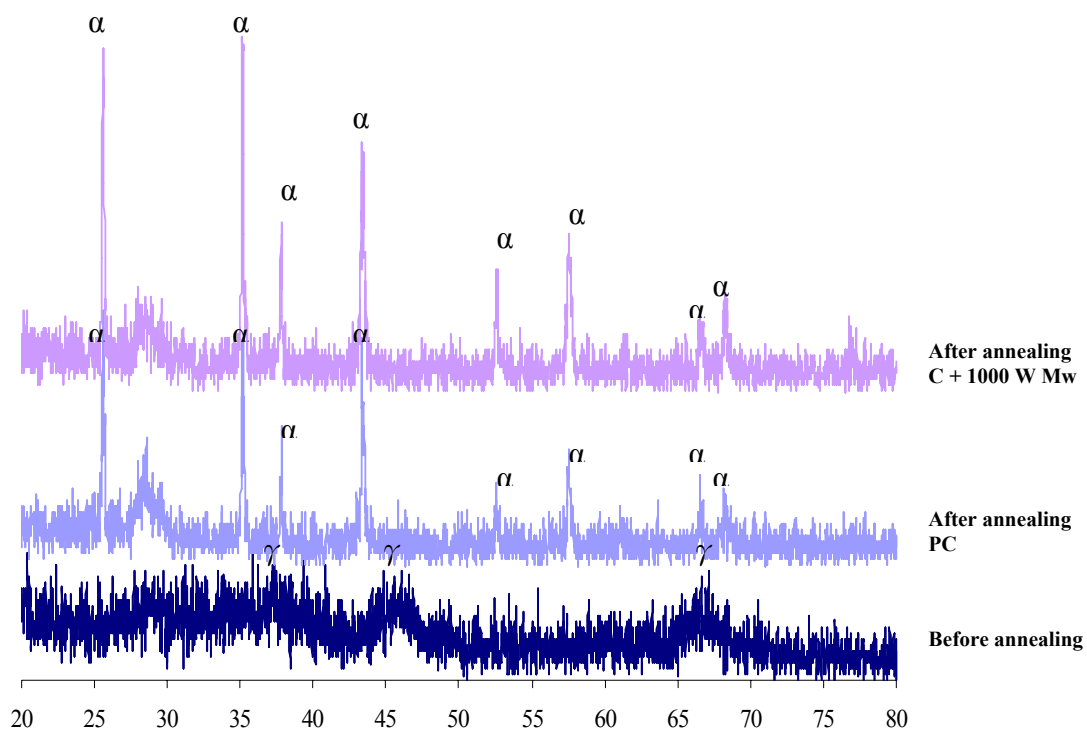


Figure 4.32. X-ray diffraction pattern for sol gel alumina before annealing and after annealing.

4.2.1.4.4. Silica

An increase of 17% in density was obtained as a result of hybrid heating with 1000 W microwave power as shown in table 4.6.

Table 4.6. Relative densities of silica sintered at 1000 °C.

Approach	Relative density / %
PC	61
C + 1000 W mw	78
Green body	51

4.2.1.5. GRAIN GROWTH IN SINTERING

Figure 4.33 shows the X-ray diffraction pattern for ZnO powder and the ceramics sintered at 680°C, whilst figure 4.33 shows the result of the grain sizes obtained by the Scherrer equation. Table 4.7 shows the result of grain size determination by SEM examination.

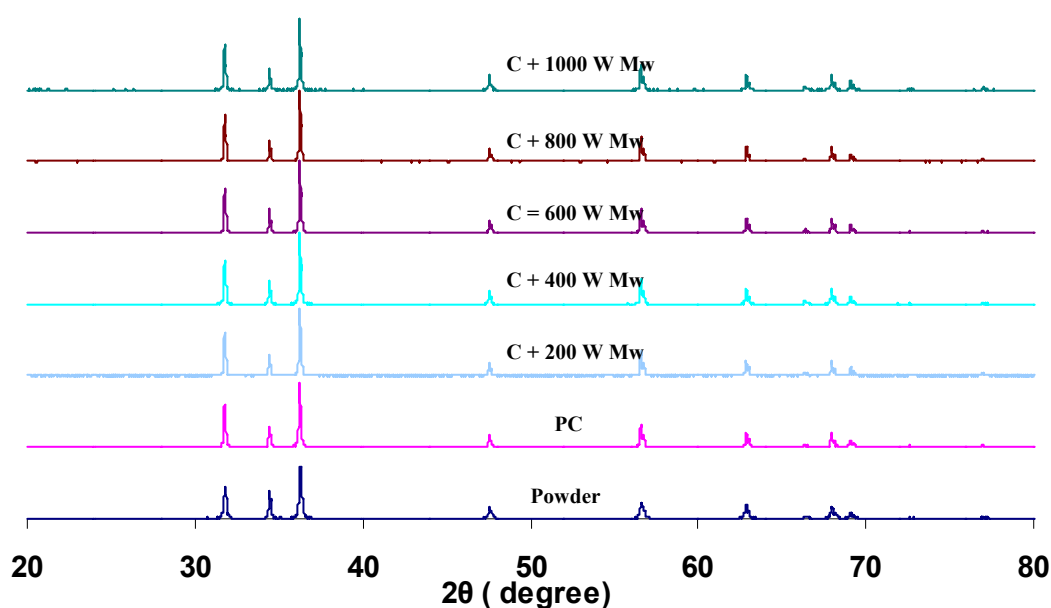


Figure 4.33a. X-ray diffraction pattern for ZnO ceramics sintered at 680 °C.

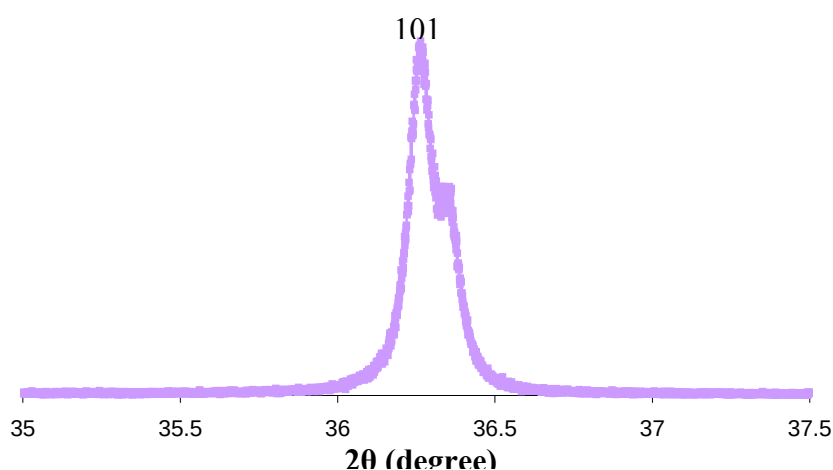


Figure 4.33b X-ray diffraction pattern of 101 plane used for the calculation of grain size.

Figure 4.34 shows that the enhanced densification was accompanied by rapid grain growth during hybrid heating.

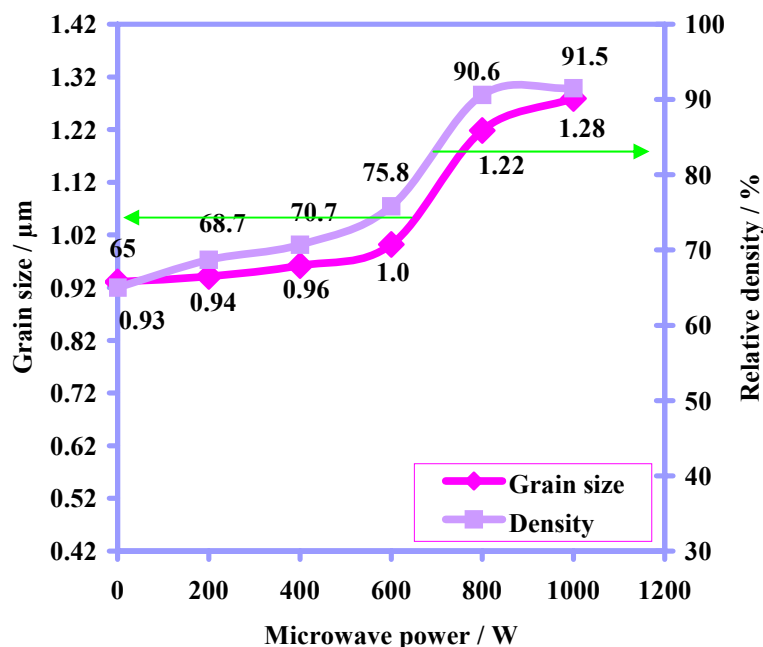


Figure 4.34. Grain size and density curves of submicron ZnO samples sintered at 680 °C using hybrid heating with different microwave power(0, 200 W, 400W, 600 W, 800 W and 1000 W) (central temperature control). The average grain size values were obtained from use of the Scherrer equation on X-ray diffraction data.

Table 4.7. Grain sizes of ZnO samples sintered at 680 °C obtained from FEG-SEM examination.

Approach	Average grain size
PC	0.26 μm
C+ 800 W Mw	0.96 μm

4.2.1.6. DENSIFICATION OBSERVATION USING A DILATOMETER

In situ densification observation of submicron ZnO pellets sintered at 680°C in pure conventional heating (PC) and hybrid heating with 600 W mw power showed that the onset of the sintering process occurred ~20mins earlier and that densification proceeded more rapidly, figure 4.35.

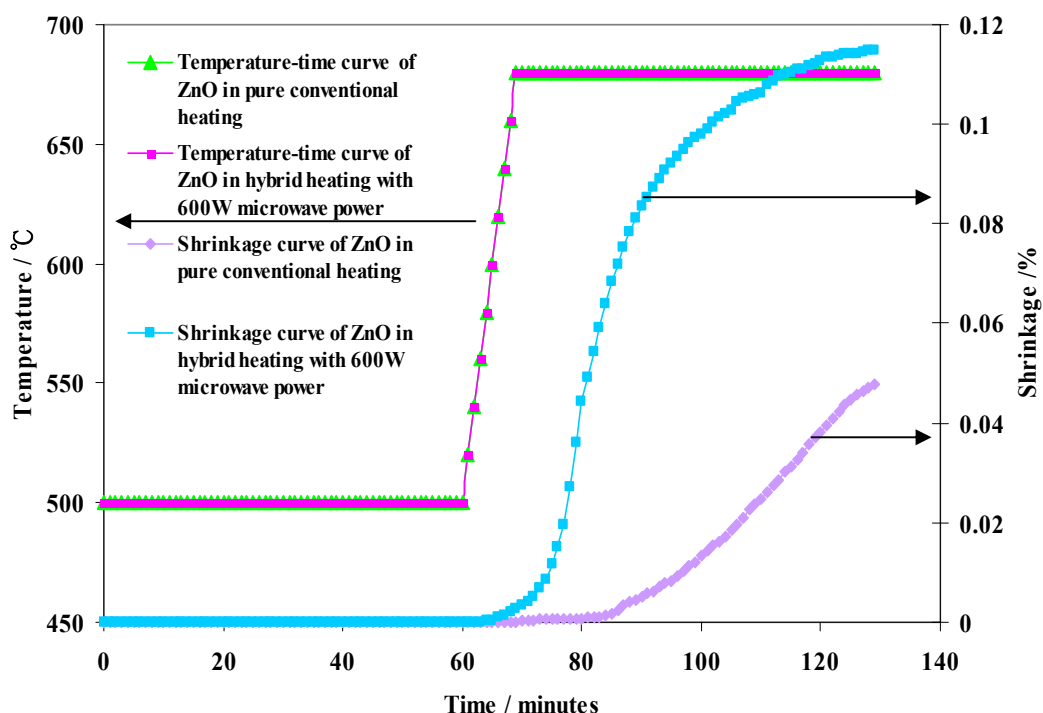
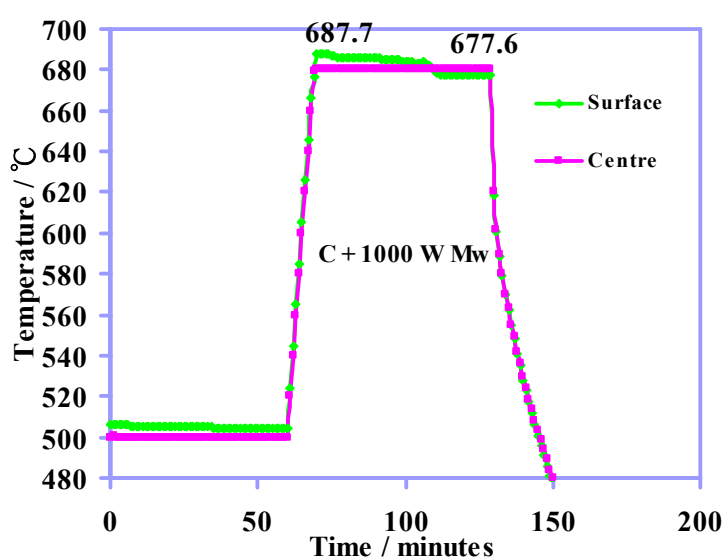


Figure 4.35. Sintering and densification curves of submicron ZnO pellets sintered at 680 °C using PC and hybrid heating with 600 W mw power.

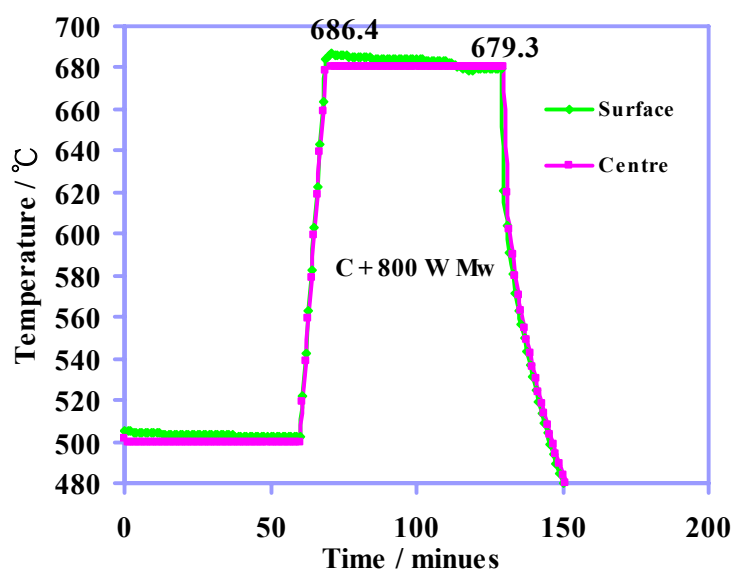
4.3. TEMPERATURE GRADIENTS

4.3.1. THE USE OF TWO OPTICAL FIBRE THERMOMETER PROBES

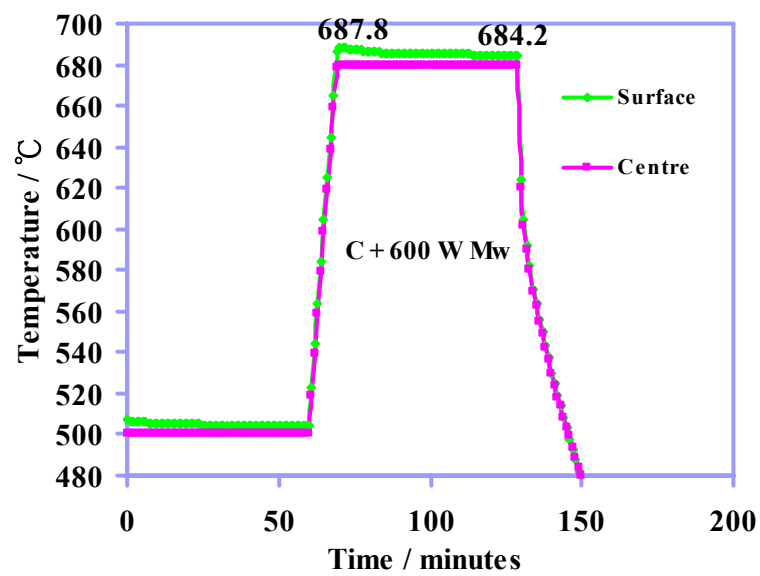
Figure 4.36 and table 4.8 show the temperature – time profiles and temperature differences between the surface and centre for submicron ZnO pellets measuring 13 mm in diameter by 5 mm in thickness which were sintered at 680°C using different microwave power levels. The biggest temperature difference was about 10°C and appeared with pure conventional heating.



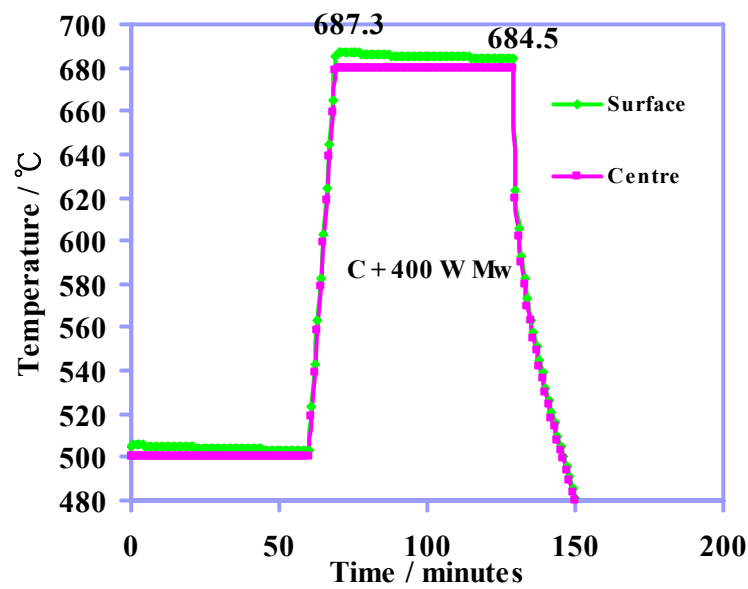
a: Conv. + 1000 W mw power.



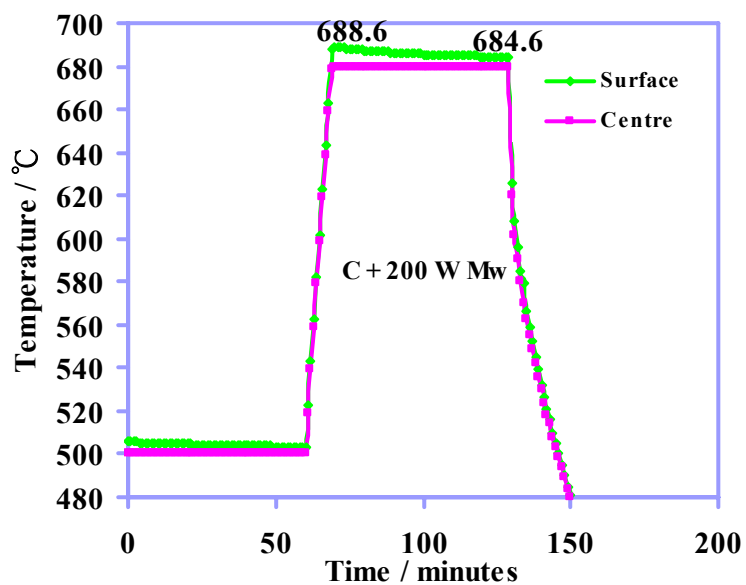
b: Conv. + 800 W mw power.



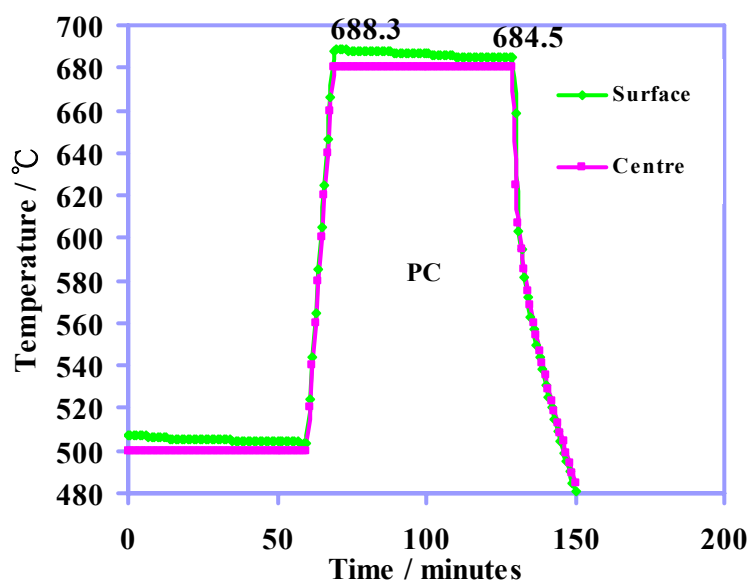
c: Conv. + 600 W mw power.



d: Conv. + 400 W mw power.



e: Conv. + 200 W mw power.



f: Pure conventional power.

Figure 4.36. Temperature-time curves for submicron ZnO pellets measuring $\text{Ø}13 \times 5$ mm, sintered at 680°C for 1 hour using different microwave power levels. The surface and central temperatures were recorded.

Table 4.8. Temperature gradients observed across samples ZnO ($\Phi 13 \times 5 \text{ mm}$)

POWER	Temperature difference at sintering temperature ($\Delta T = T_s - T_c$)	
	Starting	End
Conv. + 1000 W mw	8°C	- 3°C
Conv. + 800 W mw	6°C	- 1°C
Conv. + 600 W mw	8°C	4°C
Conv. + 400 W mw	7°C	5°C
Conv. + 200 W mw	8°C	5°C
Pure conv.	10°C	5°C

T_s is the temperature of the sample surface;

T_c is the temperature of the sample centre

Figure 4.37 show the temperatures at the surface and centre of a ZnO pellet with 25 mm diameter. The rapid decrease of the side surface temperature near the end of sintering is believed to indicate the onset of thermal runaway. Since temperature control was based on the centre of the sample it could not change; however the reduction in microwave power required to maintain the central temperature caused a sharp decrease in the surface temperature.

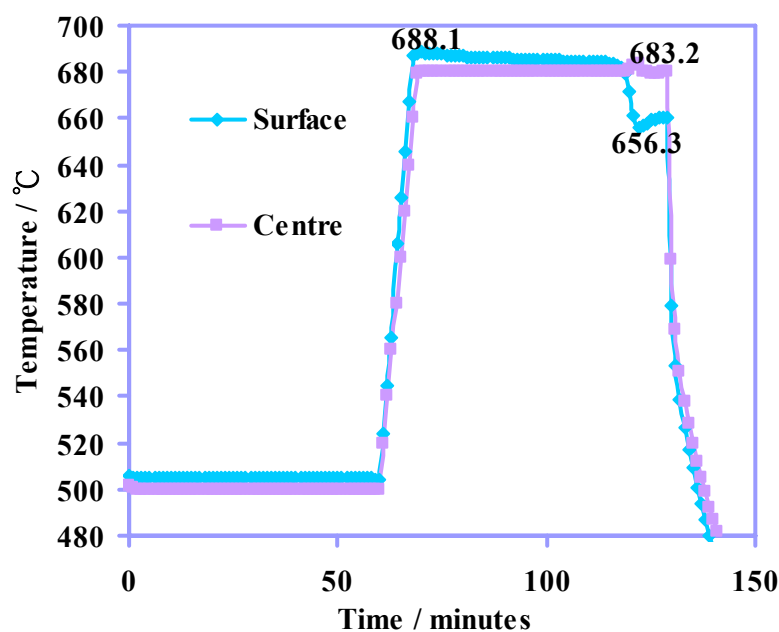


Figure 4.37. Sintering curves of ZnO pellets with a size of $\Phi 25 \text{ mm} \times 5 \text{ mm}$ sintered at 680°C (central temperature control).

4.3.2. THE EXAMINATION OF MICROSTRUCTURES

Figures 4.23 and 4.24 illustrate microstructures obtained from polished samples of the submicron ZnO pellets sintered at 680°C. All the areas showed similar microstructures in the ZnO pellet with a size of $\Phi 13\text{mm} \times 5\text{ mm}$ as shown in figure 4.38 whereas bigger grains occurred in the region between the centre and the edge of the pellet with a size of $\Phi 25\text{mm} \times 5\text{ mm}$ as shown in figure 4.39. This suggests that the centre might not be the hottest area in a large sample.

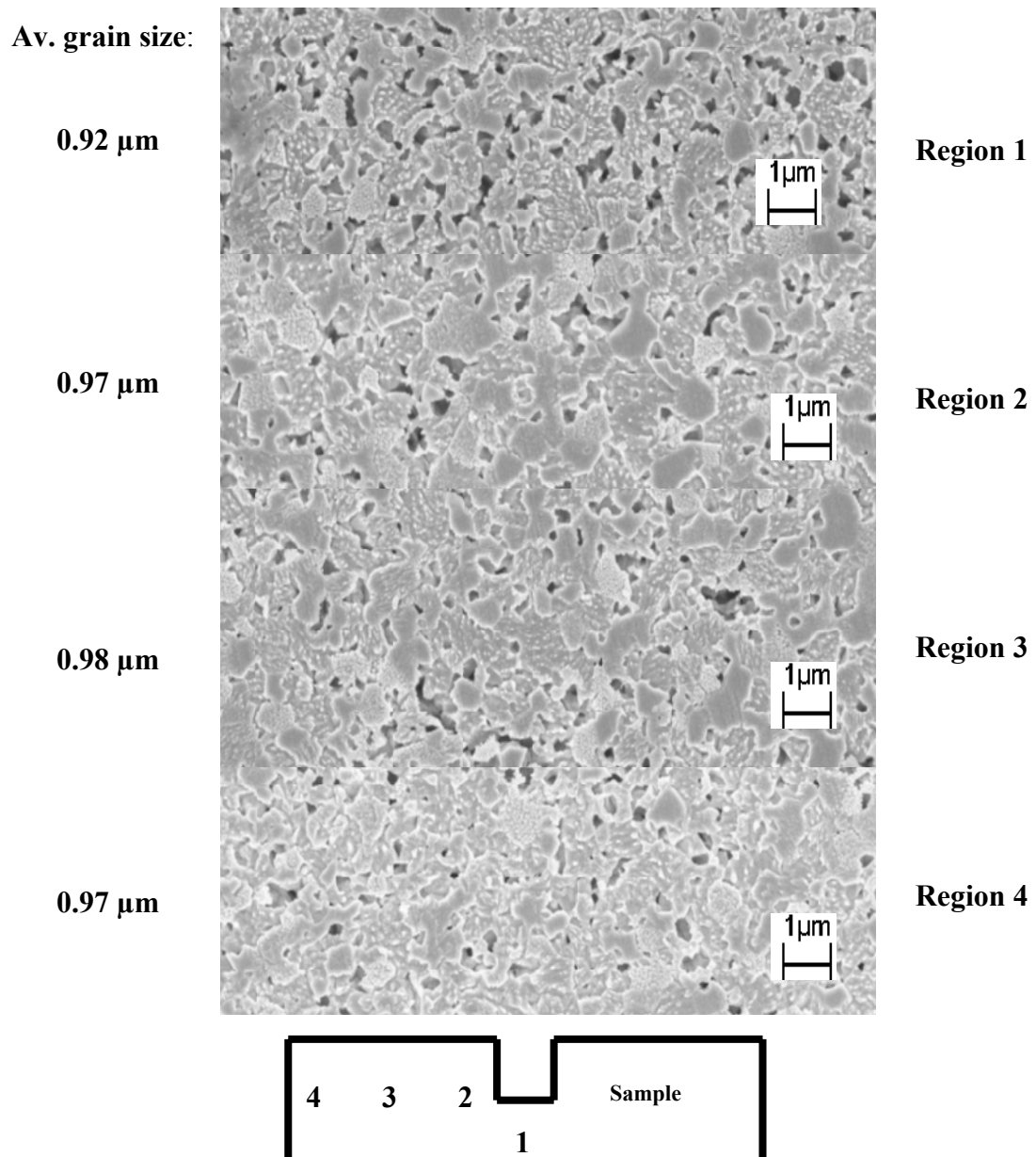


Figure 4.38. FEGSEM micrographs of cross section of a submicron ZnO pellet with a size of $\Phi 13\text{mm} \times 5\text{ mm}$ sintered at 680 °C using hybrid heating with 800 W microwave.

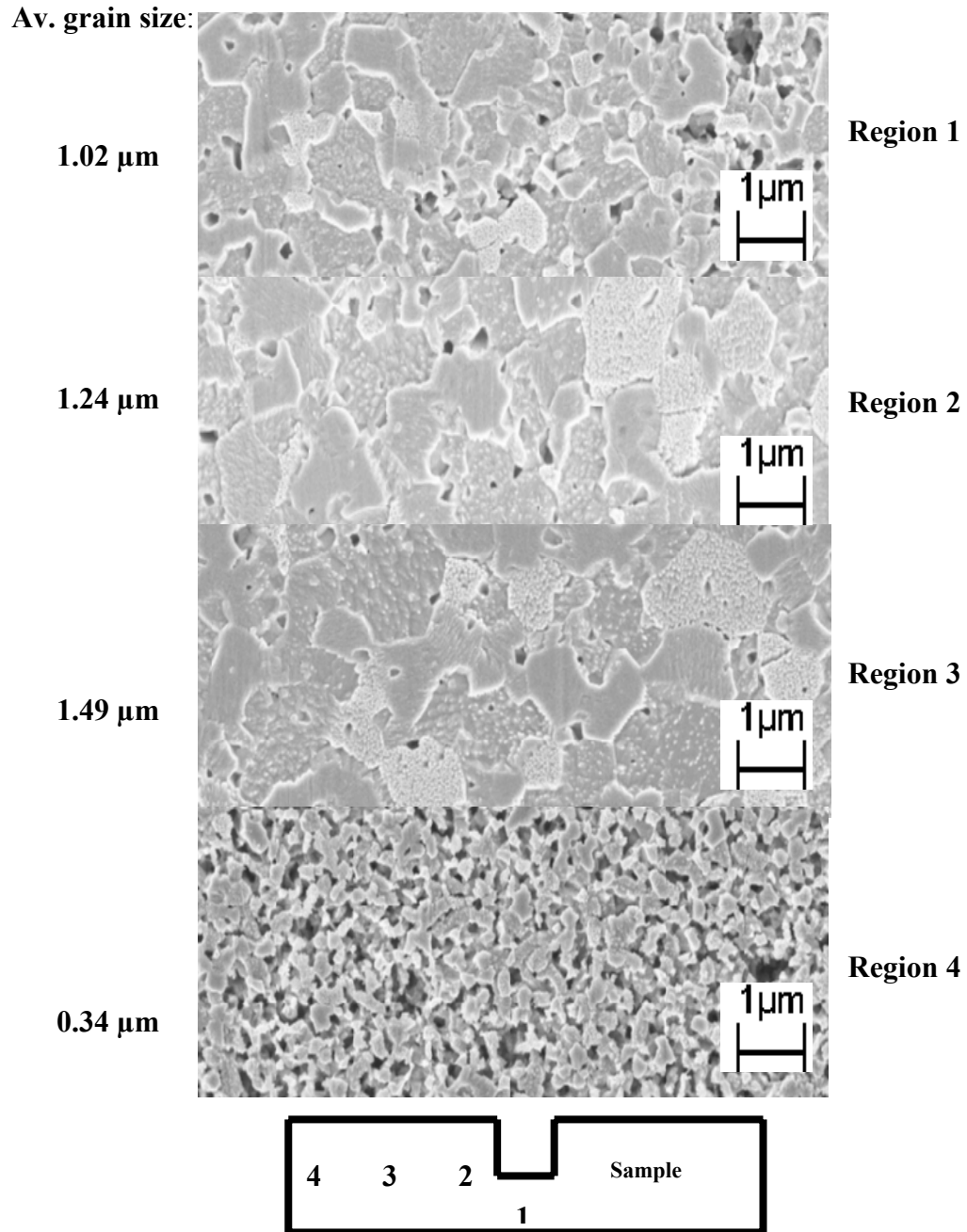


Figure 4.39. FEGSEM micrographs of cross section of a (submicron) ZnO pellet with a size of $\Phi 25\text{mm} \times 5\text{mm}$ sintered at 680°C using hybrid heating with 600 W microwave power.

4.3.3. THERMAL IMAGING

Figures 4.40 and 4.41 show thermal images of the surfaces and the temperature distributions cross the surfaces in sintered ZnO pellets with 13 mm diameter during pure conventional heating and hybrid heating with 1000 W microwave power. The highest temperature gradient was found with pure conventional heating, which was

14°C. Hybrid heating showed a lower average temperature compared to pure conventional heating. An inverse temperature profile was also observed near the end of sintering with hybrid heating, as shown in figure 4.40.

Figure 4.42 shows a thermal image of the top surface of a ZnO pellet with 25 mm diameter during hybrid heating with 600 W microwave power. A hot ring, the hottest area, between the centre and the side surface during sintering was observed, supporting the result of the microstructure observation shown in figure 4.39.

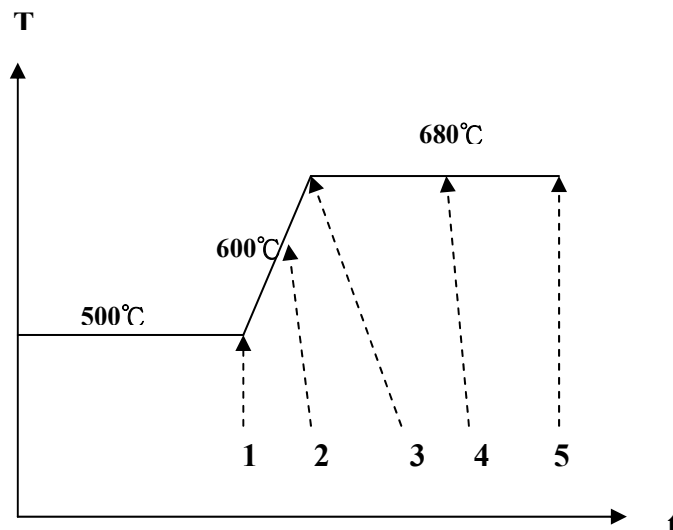


Figure 4.40a. The five observed points in the temperature-time curve.

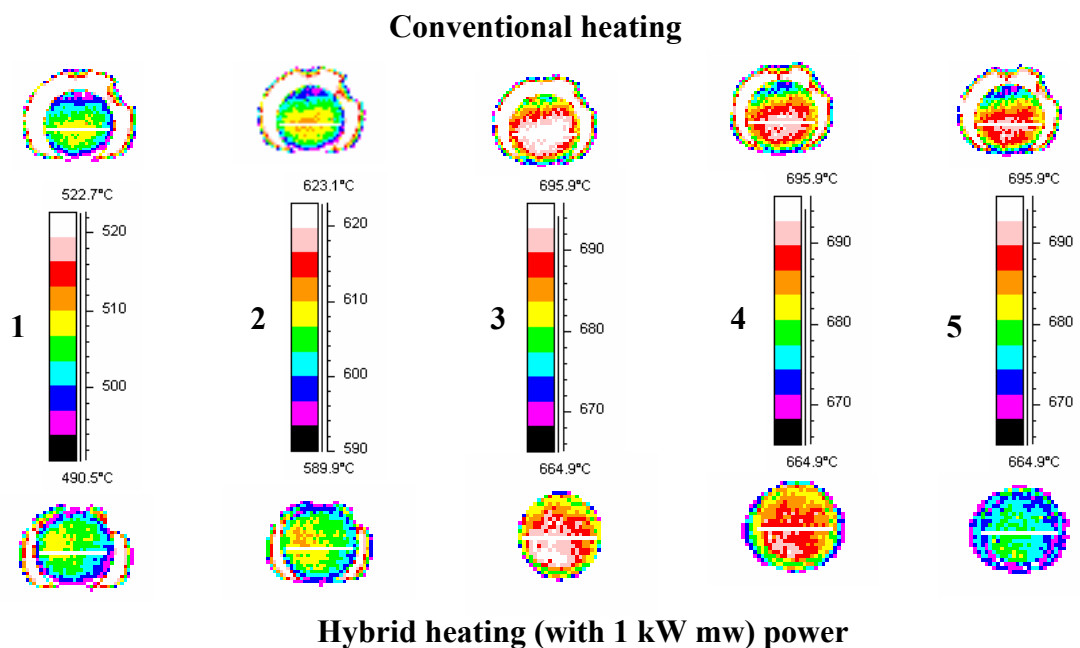
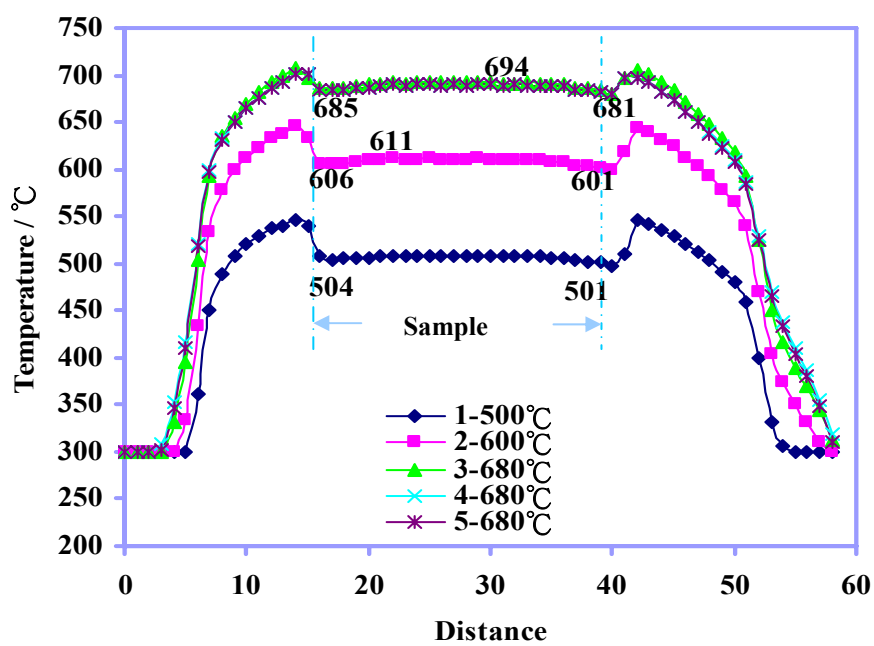
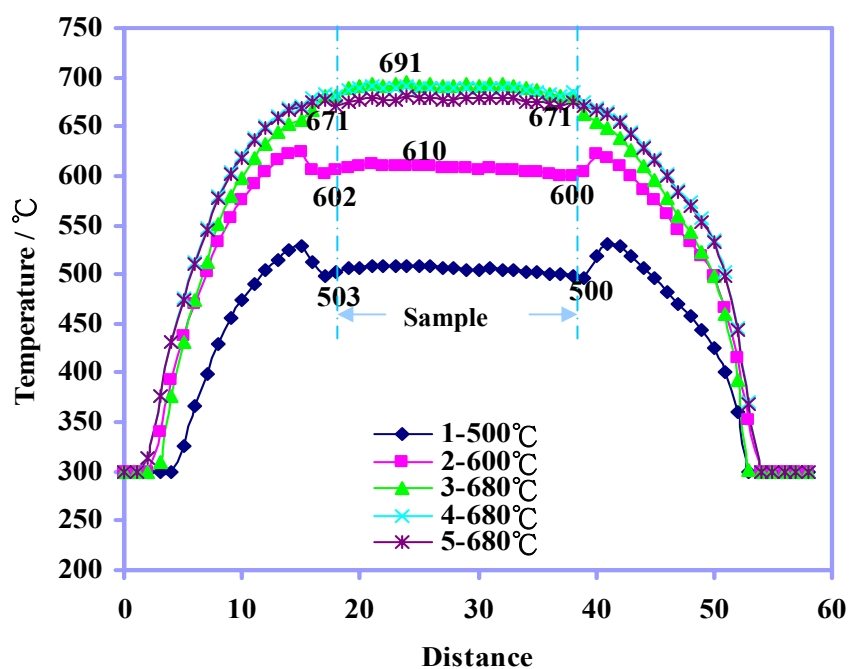


Figure 4.40b. Thermal images of the top surface of a ZnO pellet sintered at 680 °C with pure conventional heating and hybrid heating with 1000 W microwave power.



a



b

Figure 4.41. Temperature distributions cross the surfaces of ZnO pellets sintered 680 °C in (a) pure conventional heating and (b) hybrid heating with 1000 W microwave power.(The observed points were the same with figure 4.40).

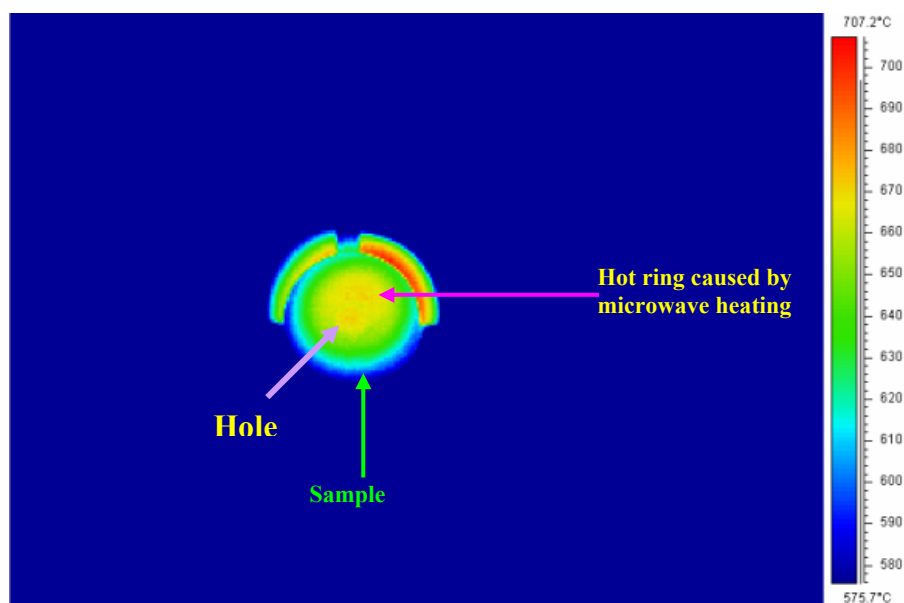


Figure 4.42. Thermal images of top surfaces of a 25 mm diameter ZnO pellet with a hole sintered at 680 °C.

The same approach described earlier in this section was used to monitor the temperature differences between the centres and the surfaces of the samples for other materials as shown in table 4.9. It can be seen that all temperature differences were <15°C except for the nano-alumina pellets sintered at 1400°C.

Table 4.9. Maximum temperature differences in the pellets during conventional heating and hybrid heating with 1000 W microwave power.

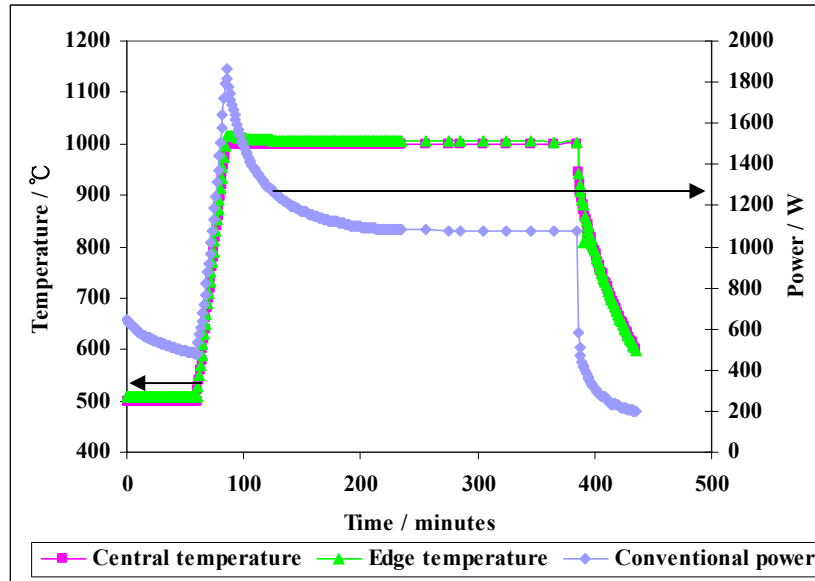
Materials	Approach	Sintering temperature / °C	Maximal temperature difference during sintering ($\Delta T = T_s - T_c$) / °C
Submicron 3-YSZ MEL	C + 1 kW mw	1220	10
	PC		11
	C + 1 kW mw	1260	10
	PC		11
Submicron 10-YSZ MEL	C + 1 kW mw	1220	11
	PC		12
	C + 1 kW mw	1260	11
	PC		14
Sol-gel alumina Synthesized	C + 1 kW mw	1180	11
	PC		12
	C + 1 kW mw	1260	10
	PC		13
Nano alumina Sigma-Aldrich	C + 1 kW mw	1400	18
	PC		23
Nano silica Sigma-Aldrich	C + 1 kW mw	1000	10
	PC		13

T_s is the temperature of the sample surface and T_c is the temperature of the sample centre.

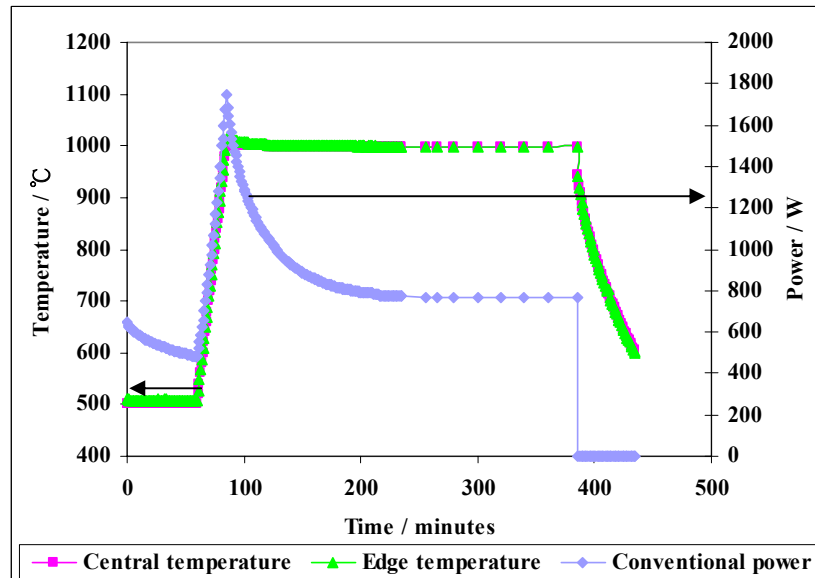
4.4. GRAIN GROWTH OF ZINC OXIDE

4.4.1. TEMPERATURE.-.TIME PROFILES

Figure 4.43 shows the annealing curves and the application of conventional power to achieve it for submicron ZnO pellets at 1000°C using pure conventional heating and hybrid heating. The annealing curves at the same annealing temperature were identical. Similar curves were also obtained at 900°C, 1050°C, 1100°C, 1150°C and 1200°C.



a: pure conventional heating

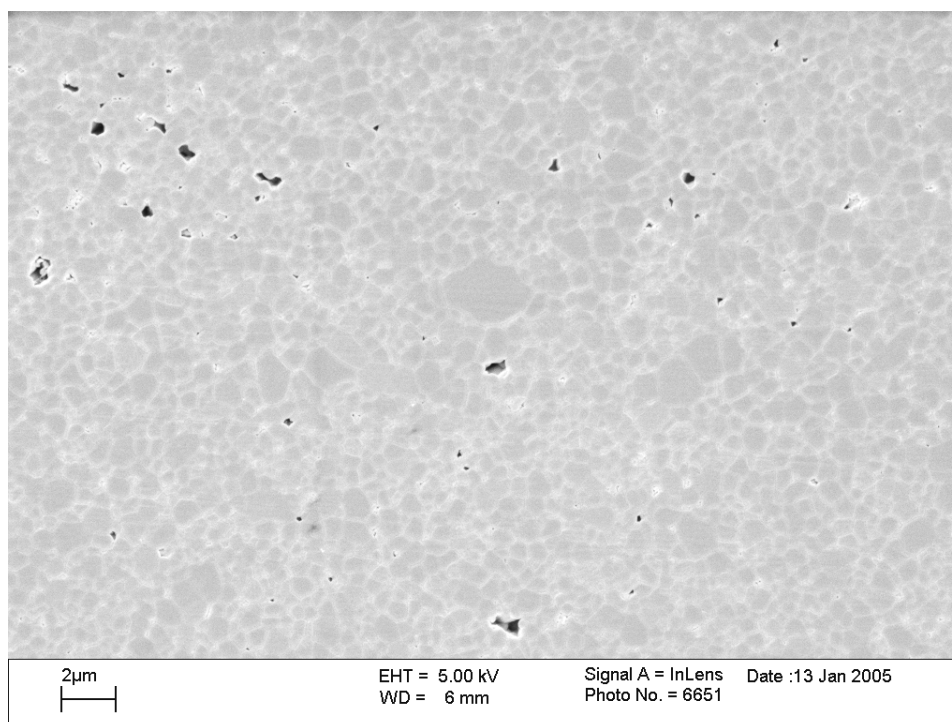


b: Hybrid heating with 1000 W microwave power

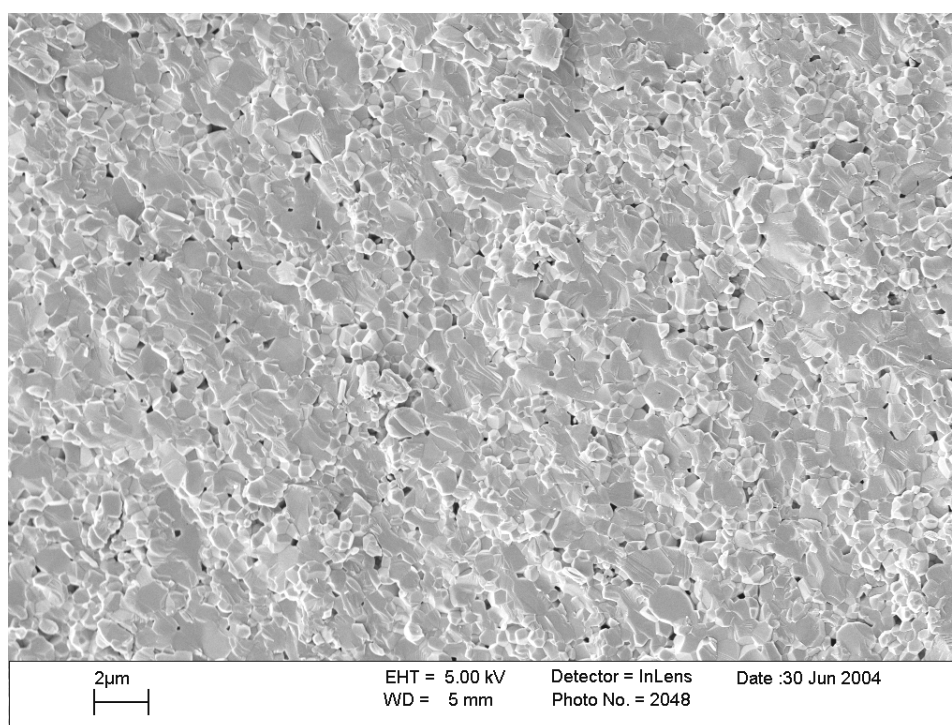
Figure 4.43. Annealing curves of ZnO pellets in pure conventional processing and hybrid processing at 1000 °C.

4.4.2. MICROSTRUCTURES AND GRAIN SIZE DISTRIBUTION

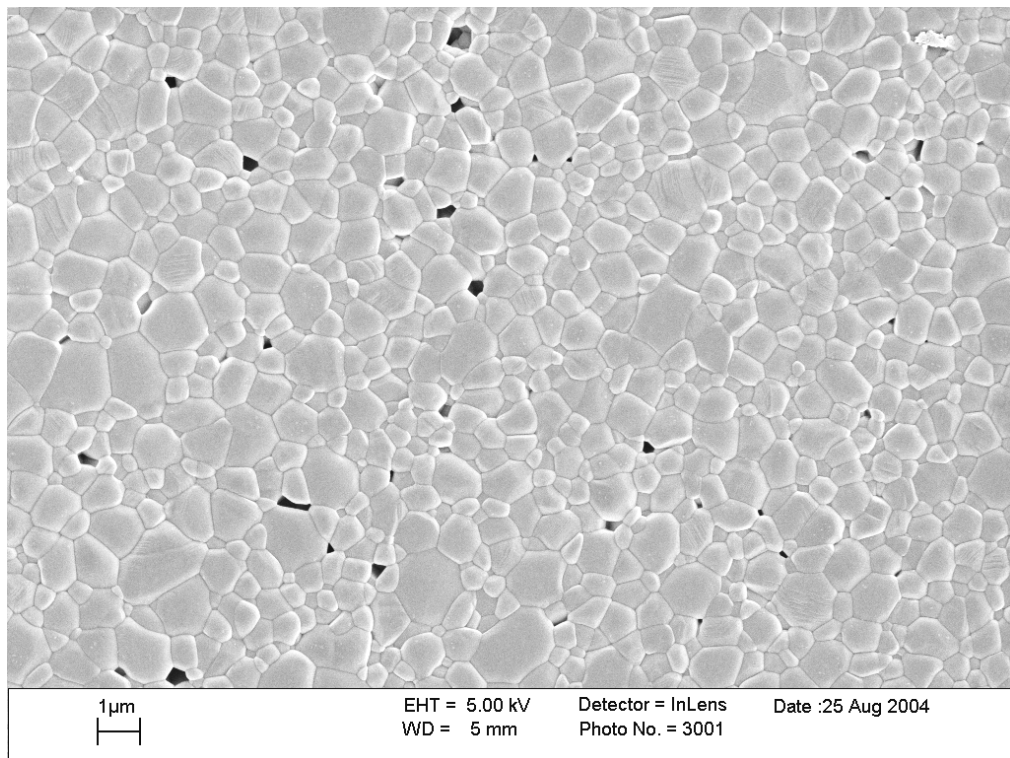
Figure 4.44 shows the microstructures of (submicron) ZnO pellets' centres before annealing and annealed at 900°C, 1000°C, 1050°C, 1100°C and 1150°C for 5 hours in pure conventional heating and hybrid heating with 1000 W microwave power. It can be seen that the grain sizes in the samples annealed in hybrid heating were bigger than those after pure conventional heating.



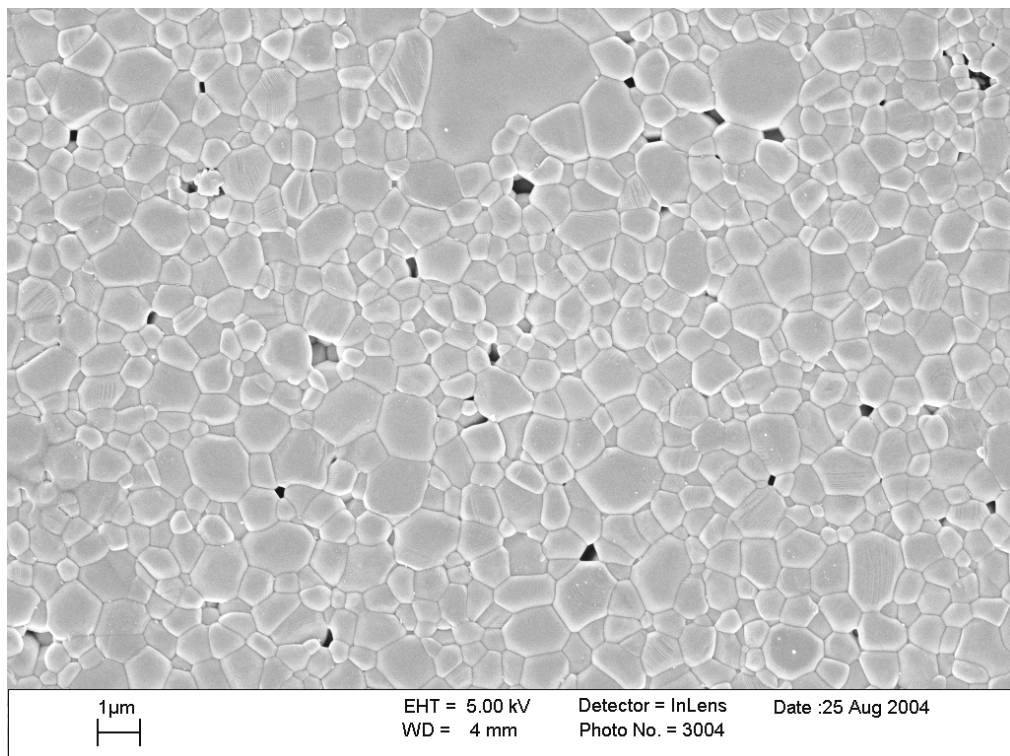
a: Polished surface of ZnO centre before annealing



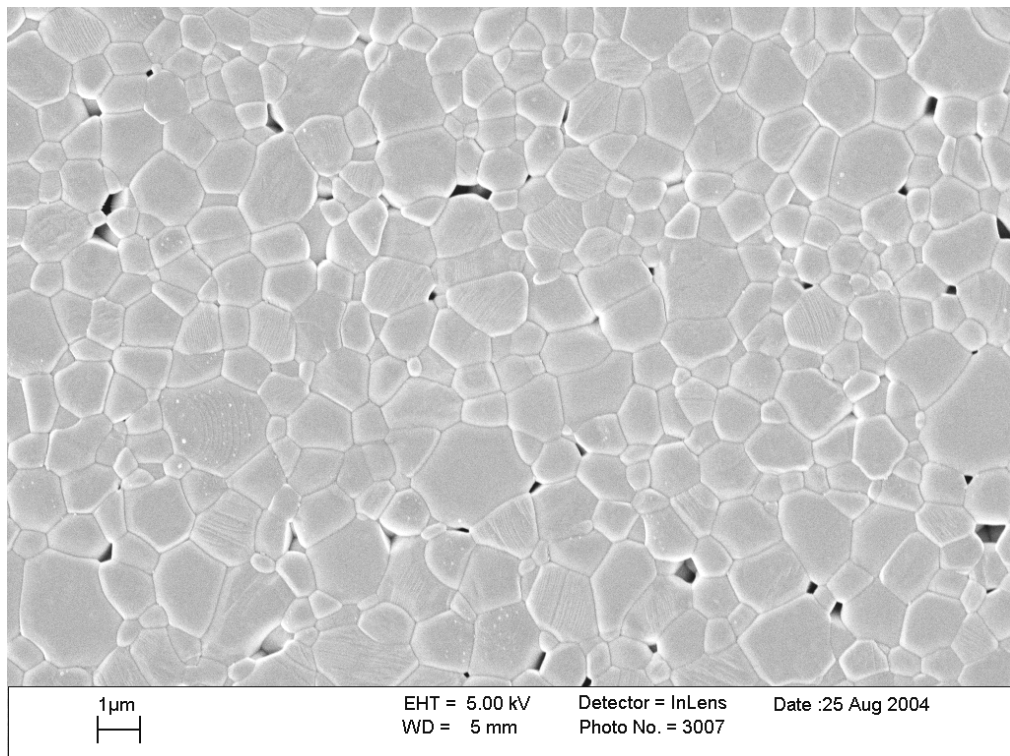
b: Fracture surface of ZnO centre before annealing



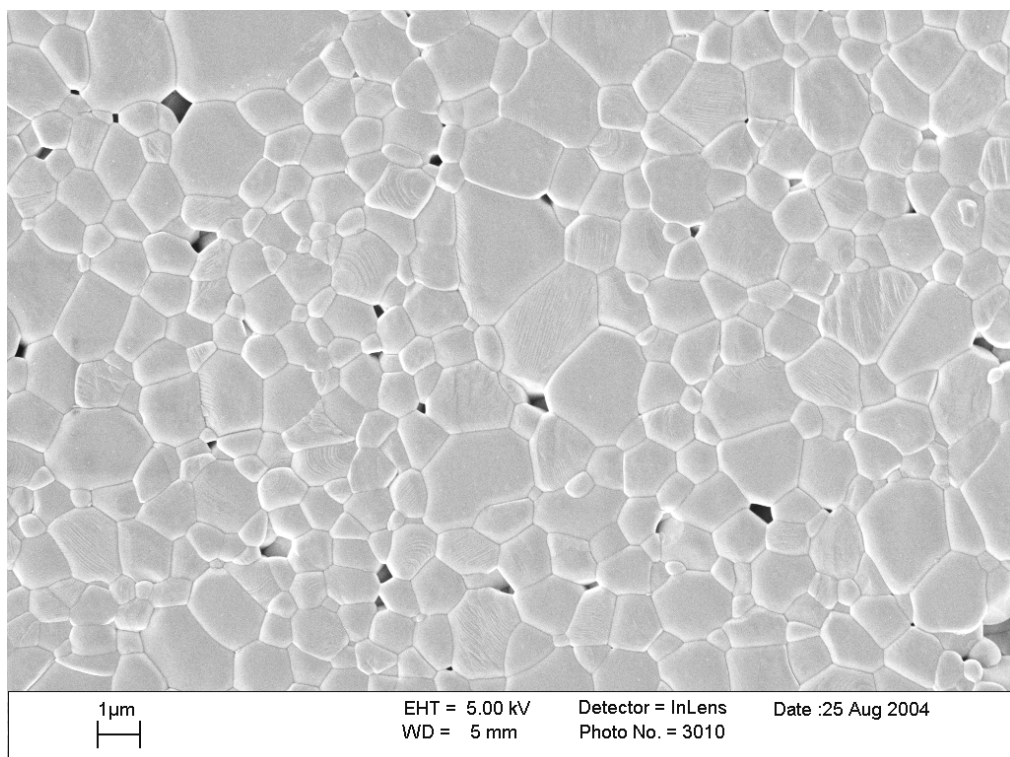
c: Annealed at 900°C using pure conventional heating



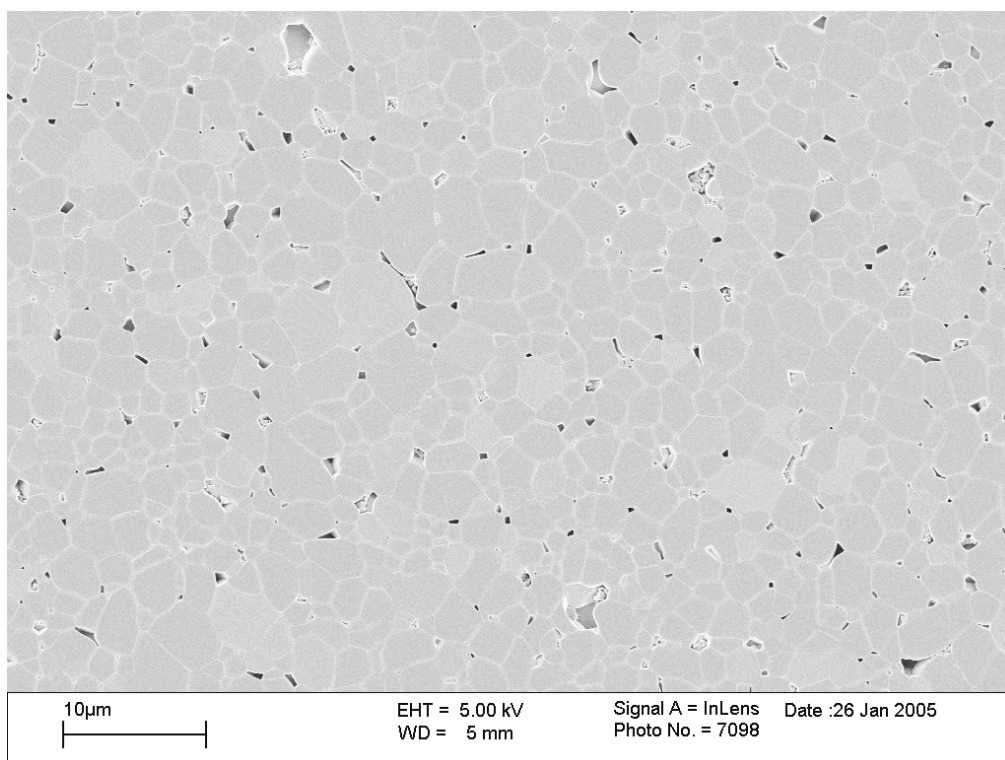
d: Annealed at 900°C using hybrid heating



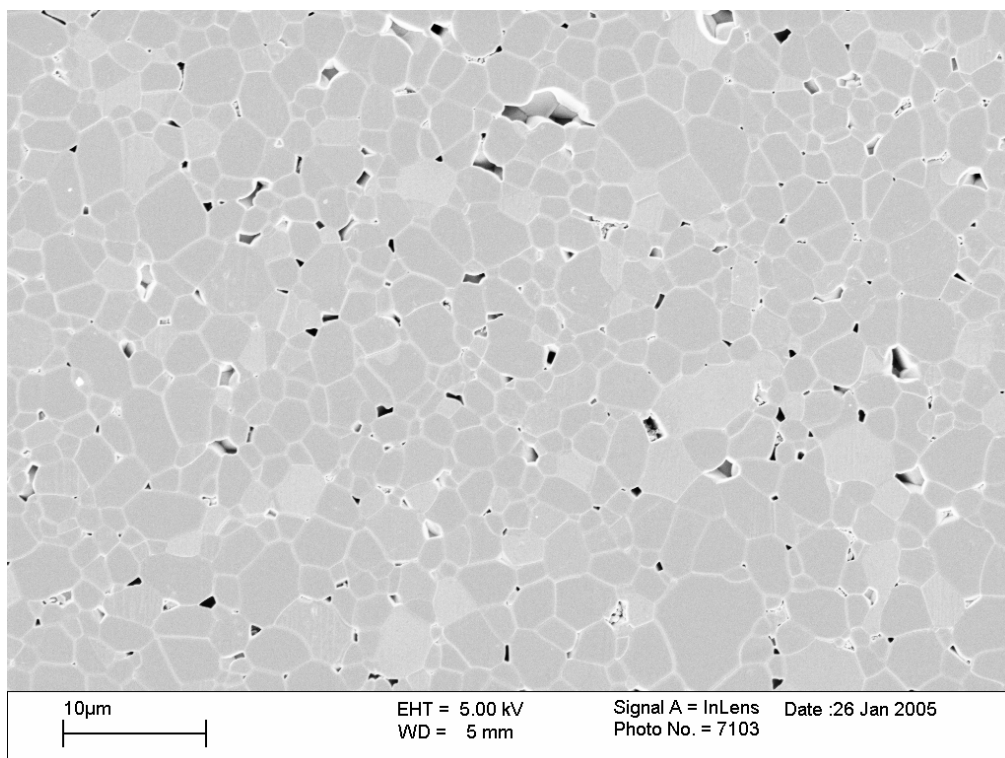
e: Annealed at 1000°C using pure conventional heating



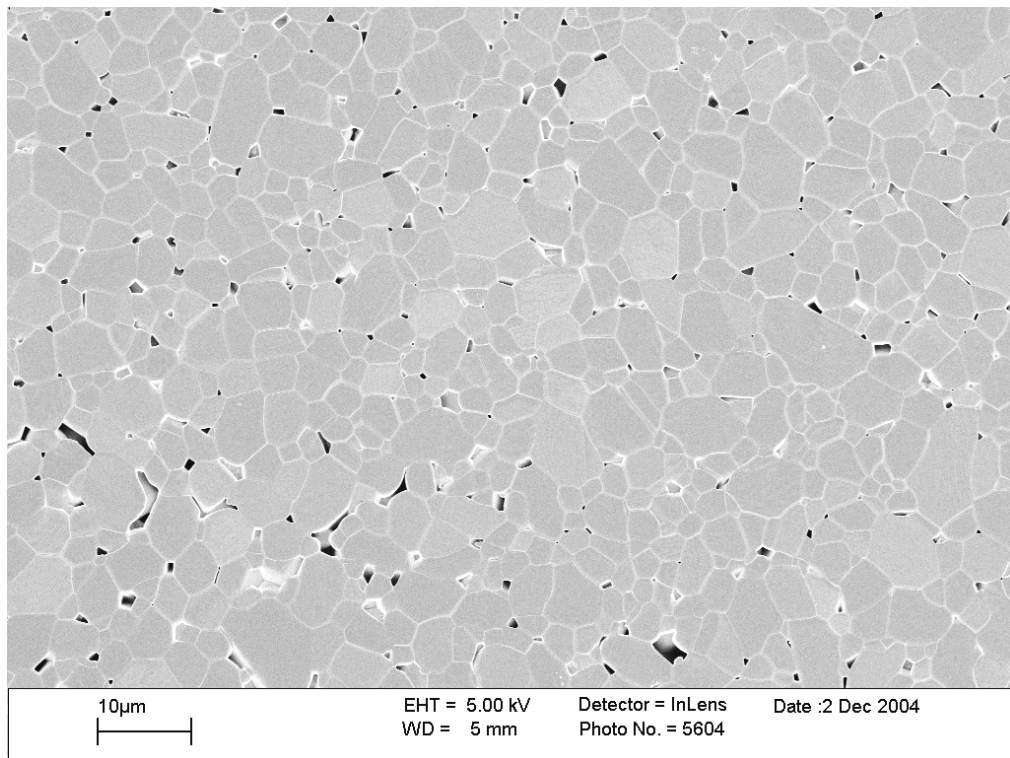
f: Annealed at 1000°C using hybrid heating



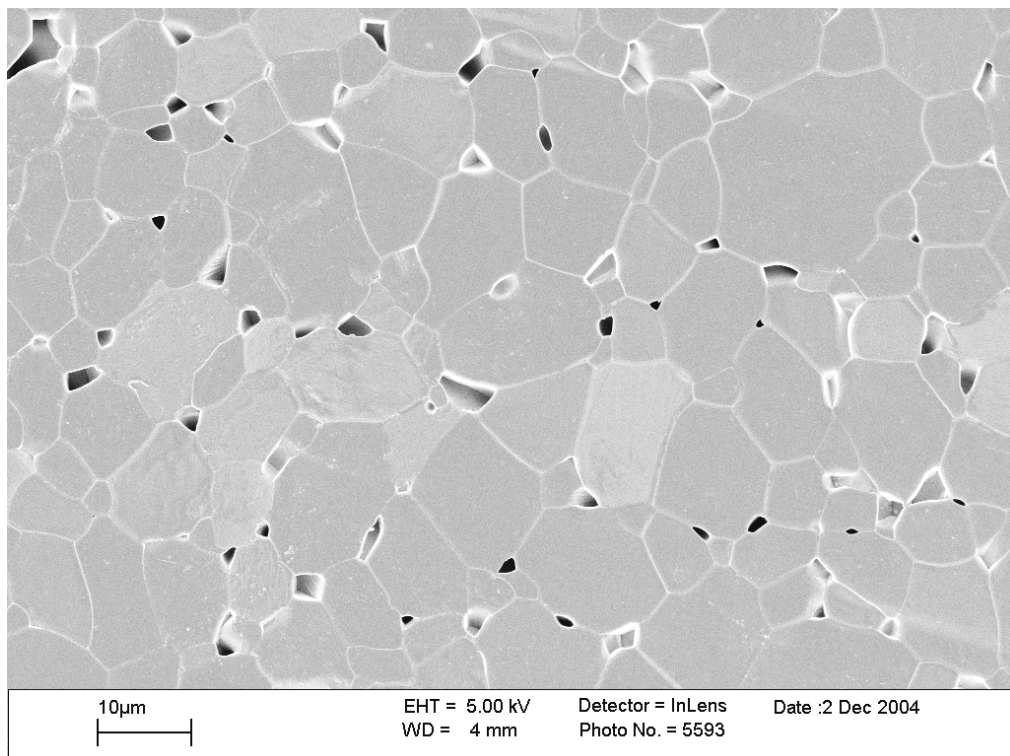
g: Annealed at 1050°C using pure conventional heating



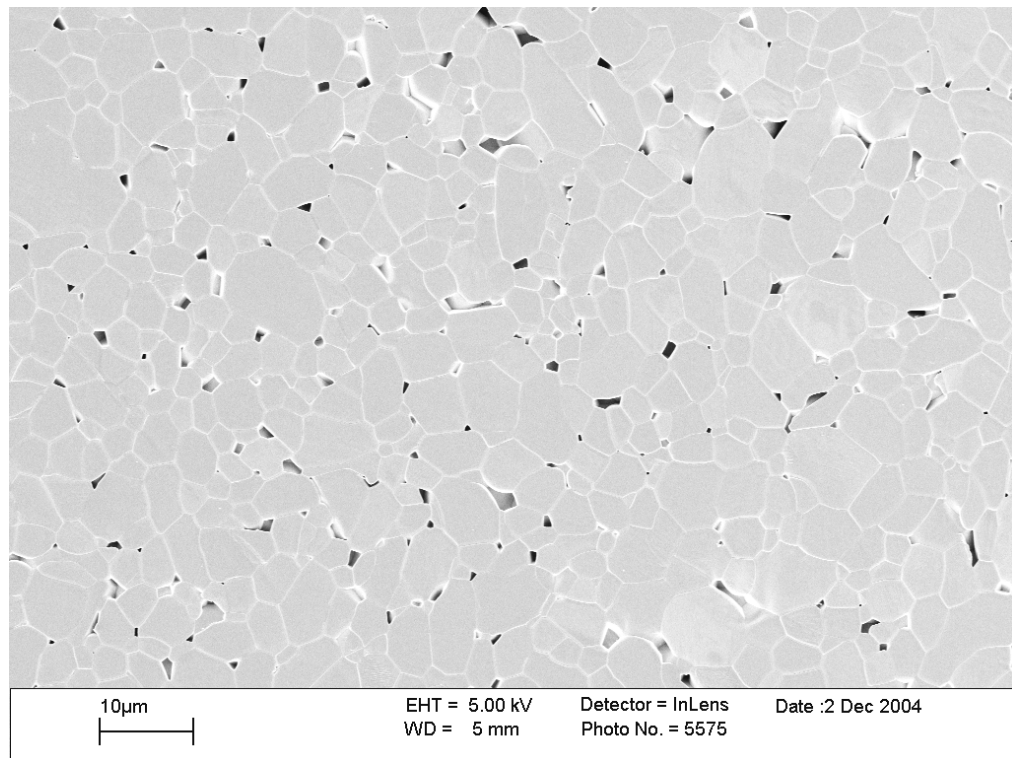
h: Annealed at 1050°C using hybrid heating



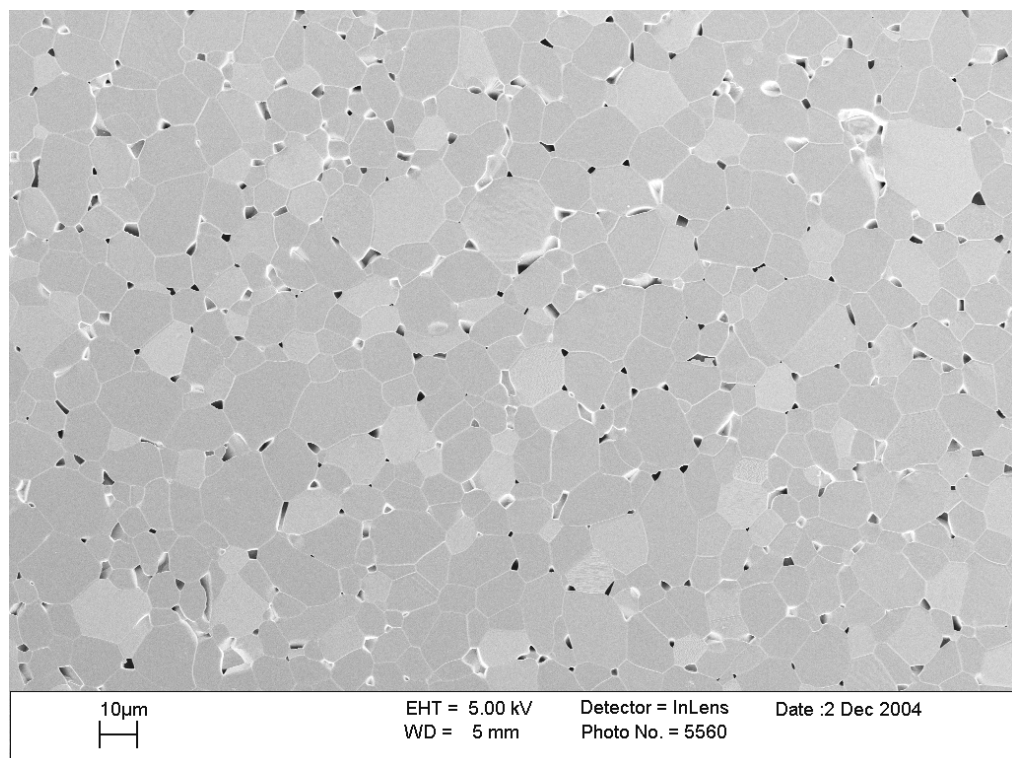
i: Annealed at 1100°C using pure conventional heating



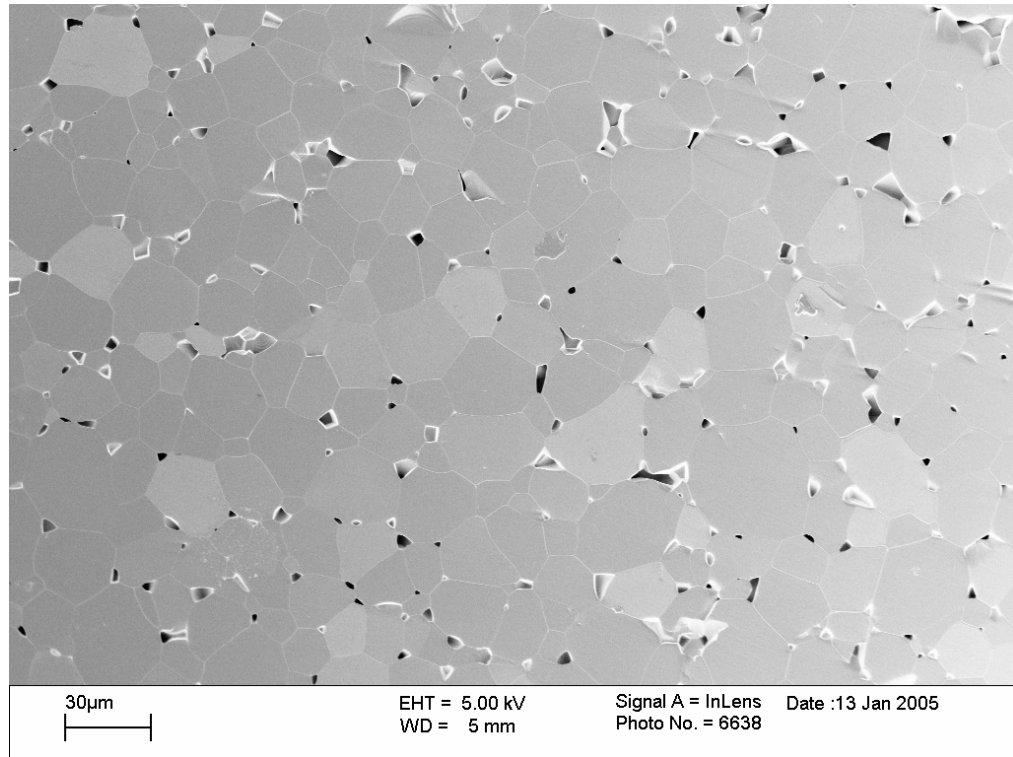
j: Annealed at 1100°C using hybrid heating



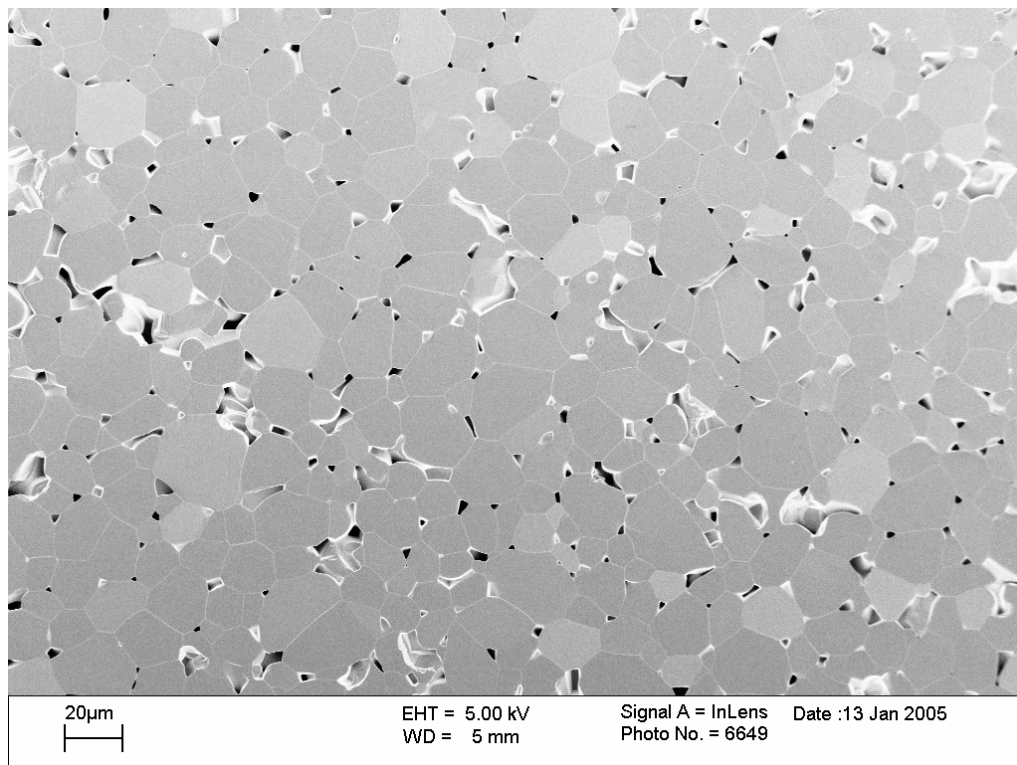
k: Annealed at 1150°C using pure conventional heating



l: Annealed at 1150°C using hybrid heating



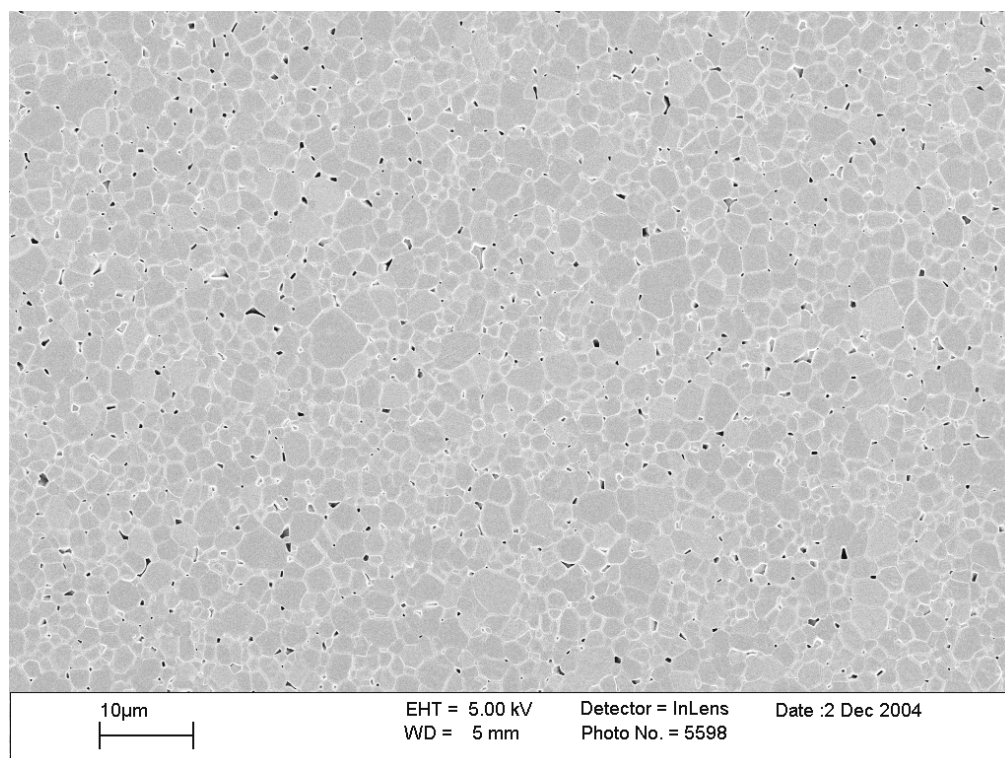
m: Annealed at 1200°C using pure conventional heating



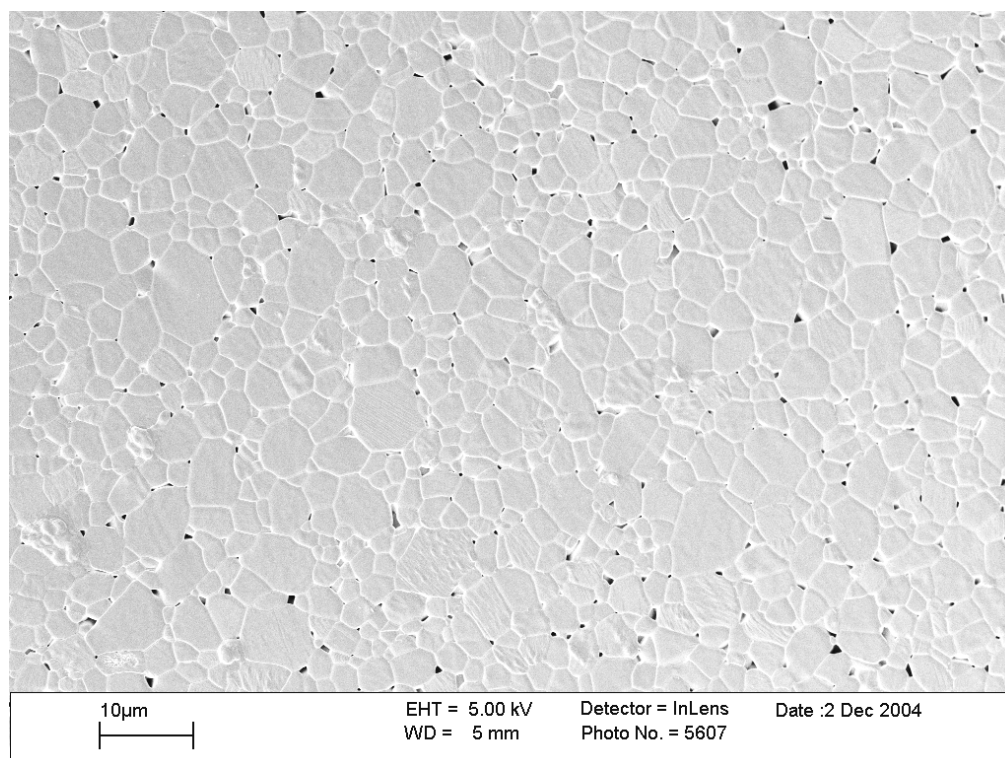
n: Annealed at 1200°C using hybrid heating

Figure 4.44. FEG-SEM micrographs of submicron ZnO pellets centres before annealing and annealed at 900 °C, 1000 °C, 1050 °C, 1100 °C, 1150 °C and 1200 °C for 5 hours using pure conventional heating and hybrid heating with 1000 W.

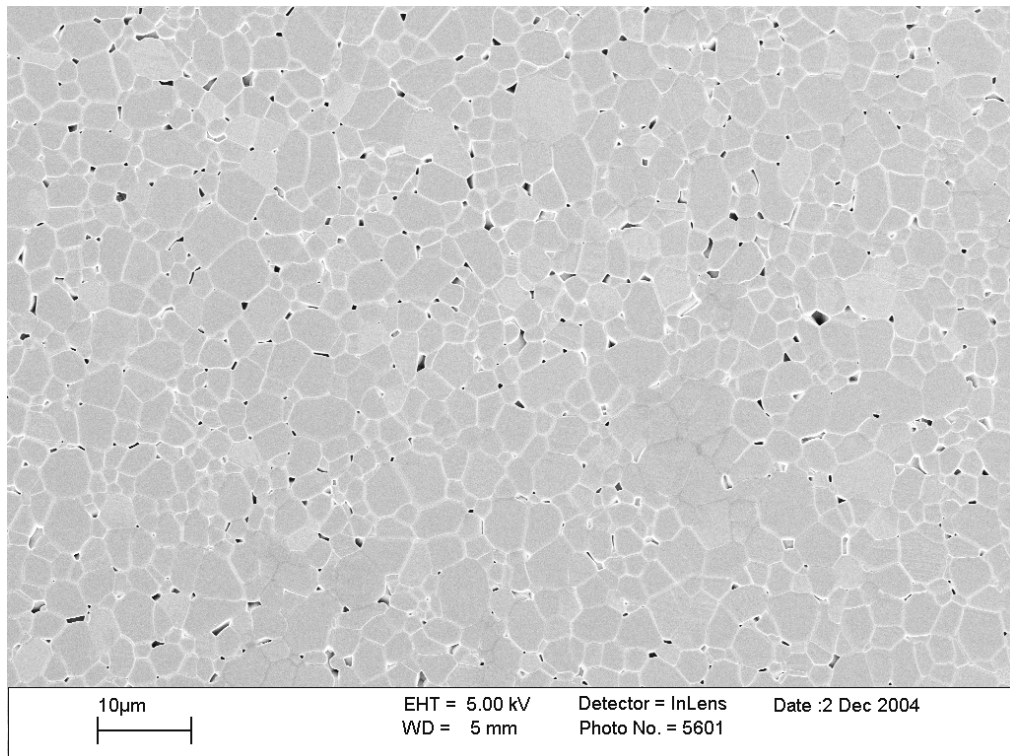
Figure 4.45 shows the microstructures of submicron ZnO pellet centres annealed at 1100°C for periods of 1, 3 and 5 hours in pure conventional heating and hybrid heating with 1000 W microwave power.



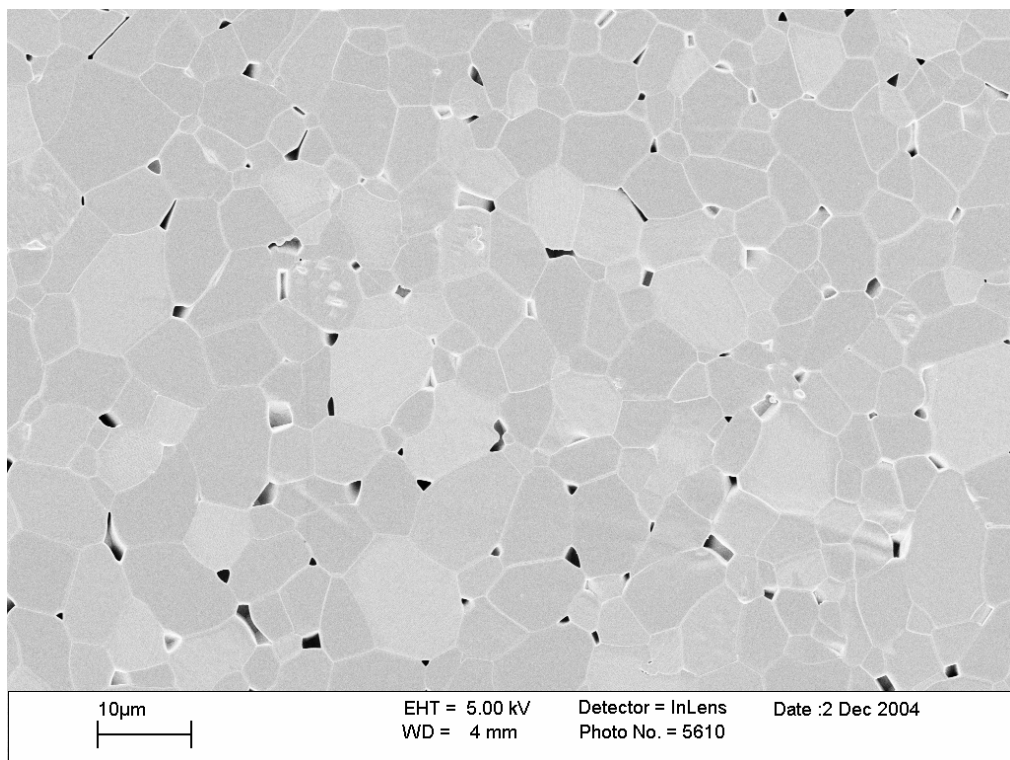
a: Annealed at 1100°C using pure conventional heating for 1 hour



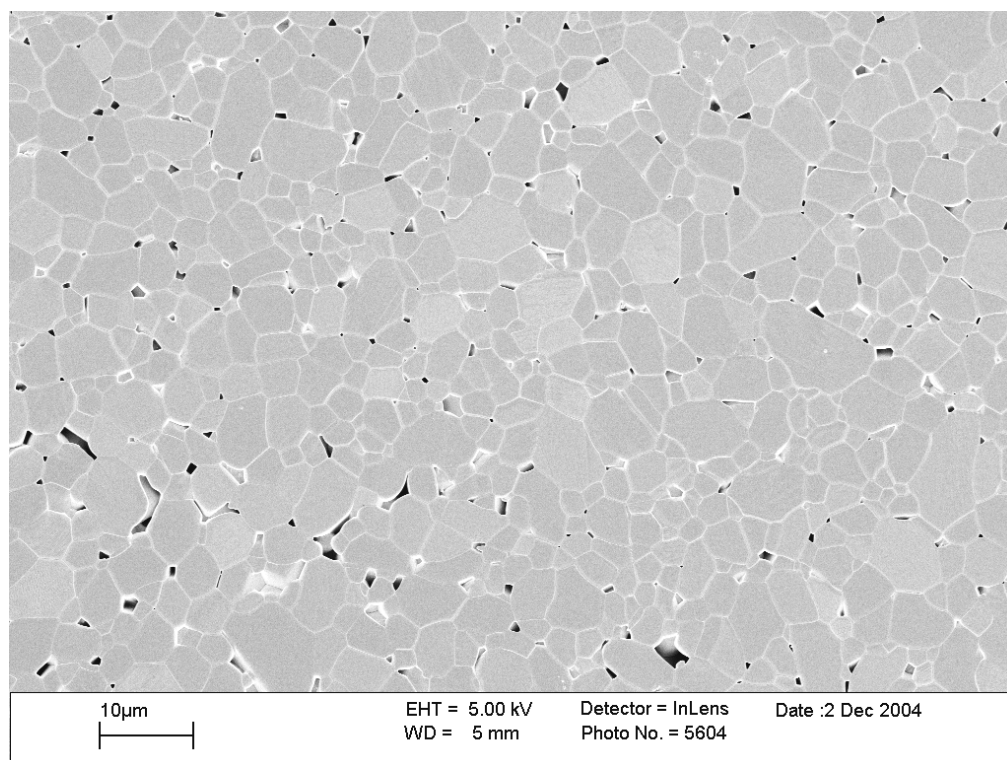
b: Annealed at 1100°C using hybrid heating for 1 hour



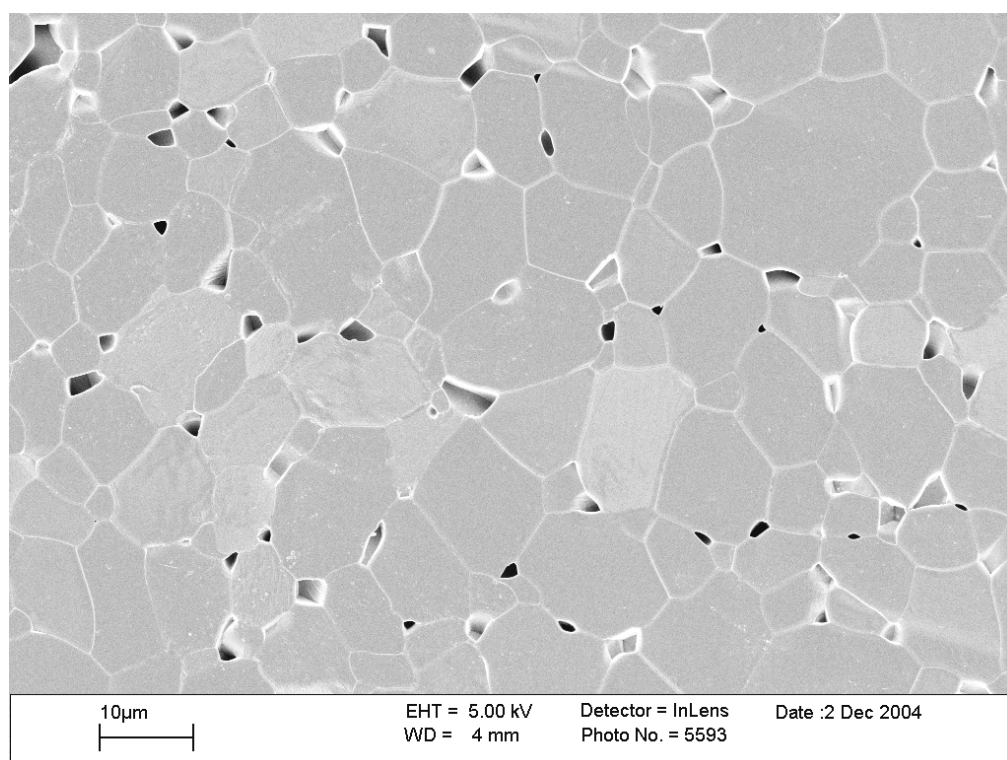
c: Annealed at 1100°C using pure conventional heating for 3 hours



d: Annealed at 1100°C using hybrid heating for 3 hours



e: Annealed at 1100°C using pure conventional heating for 5 hours



f: Annealed at 1100°C using hybrid heating for 5 hours

Figure 4.45. FEG-SEM micrographs of submicron ZnO pellet centres annealed at 1100 °C for 1, 3 and 5 hours in pure conventional heating and hybrid heating with 1000 W microwave power.

Figures 4.46 and 4.47 show the microstructures of three different regions of the ZnO pellets annealed at 1100°C and 1200°C in pure conventional heating. Whilst lower porosity and finer grains were found in the edge region of the sample, higher porosity and bigger grains were detected in the middle and central regions. More and bigger pores appeared in the sample annealed at 1200°C compared to that annealed at 1100°C.

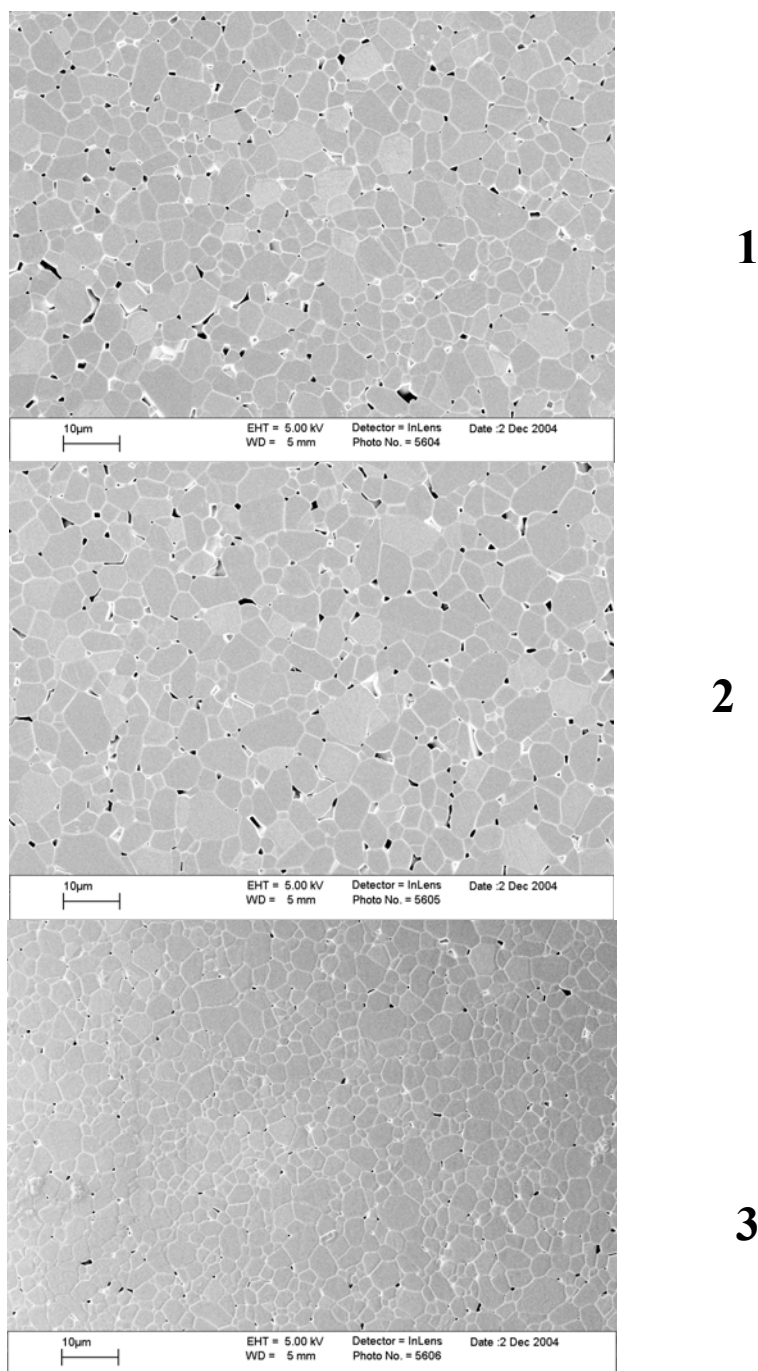


Figure 4.46. FEGSEM micrographs of submicron ZnO pellets from three different regions, 1-centre, 2-middle and 3-edge, annealed at 1100 °C for 3 hours with pure conventional heating.

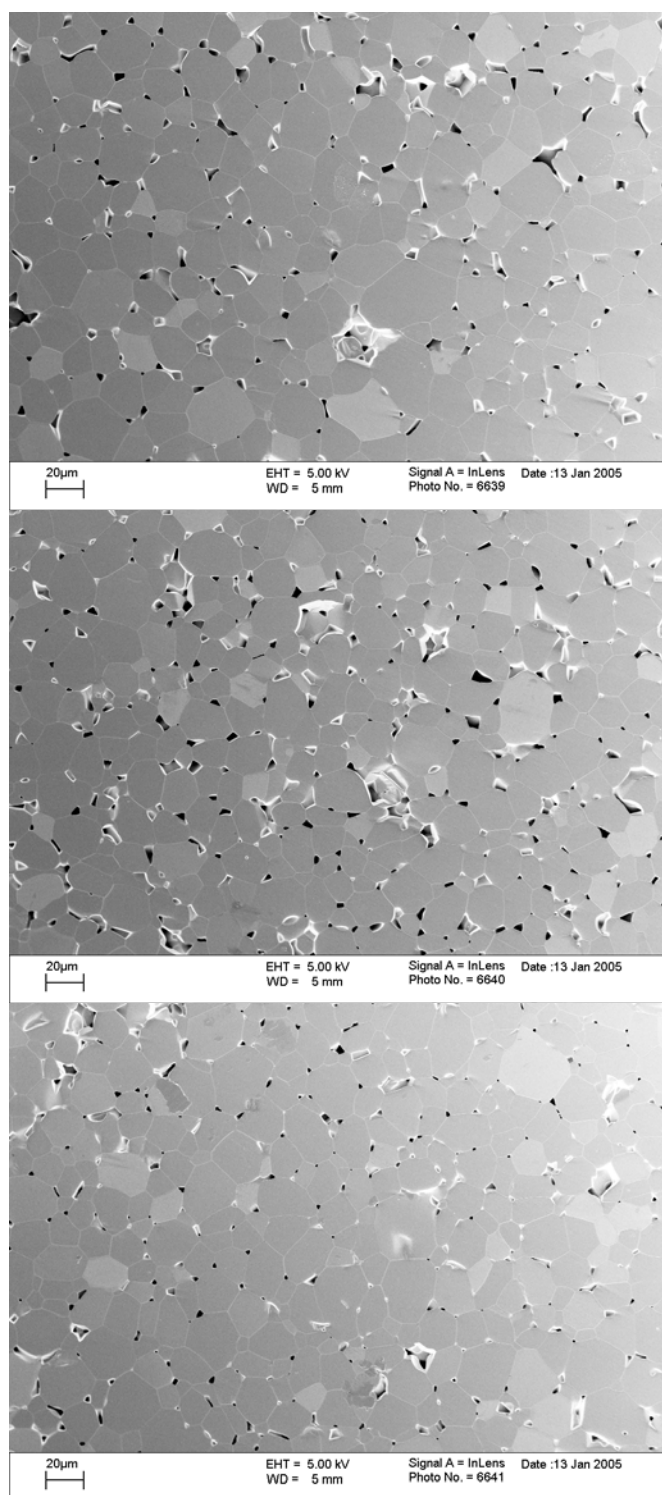


Figure 4.47. FEGSEM micrographs of three different regions, 1-centre, 2-middle and 3-edge of submicron ZnO pellets annealed at 1200 °C for 5 hours with pure conventional heating.

Table 4.10 show the grain sizes of the three different regions of the ZnO pellets at 900°C, 1000°C, 1050°C, 1100°C, 1150°C and 1200°C.

Table 4.10. The grain growth of submicron ZnO annealed at 1100 °C and 1150 °C.

Grain size / μm	PC				C + 1000 W			
	Region			Average	Region			Average
	1	2	3		1	2	3	
900°C	0.64±0.02	0.66±0.04	0.55±0.03	0.62±0.07	0.69±0.05	0.69±0.04	0.65±0.03	0.68±0.03
1000°C	0.93±0.04	0.96±0.05	0.86±0.03	0.92±0.06	1.01±0.05	1.10±0.06	0.92±0.03	1.01±0.09
1050°C	2.03±0.0	2.13±0.04	1.74±0.03	1.97±0.23	2.37±0.02	2.46±0.06	1.70±0.05	2.18±0.48

At 1100°C

Grain size / μm	PC				C + 1000 W			
	Region			Average	Region			Average
	1	2	3		1	2	3	
1 h	1.90±0.03	2.01±0.03	1.61±0.01	1.84±0.23	2.85±0.06	2.97±0.05	2.66±0.02	2.83±0.17
3 hs	2.62±0.05	2.89±0.06	2.20±0.04	2.57±0.31	6.15±0.03	7.06±0.08	5.45±0.05	6.22±1.61
5hs	3.02±0.03	3.39±0.04	2.65±0.03	3.02±0.37	8.95±0.04	9.18±0.04	8.82±0.04	8.98±0.20

At 1150°C

Grain size / μm	PC				C + 1000 W			
	Region			Average	Region			Average
	1	2	3		1	2	3	
1 h	2.26±0.03	2.76±0.03	1.88±0.04	2.30±0.46	2.90±0.04	3.04±0.03	2.77±0.05	3.03±0.26
3 hs	3.35±0.04	3.83±0.05	2.48±0.04	3.22±0.74	6.22±0.06	7.42±0.06	6.31±0.05	6.65±0.77
5 h3	3.77±0.07	3.85±0.05	3.63±0.06	3.75±0.12	9.61±0.04	9.66±0.06	9.61±0.05	9.63±0.03

At 1200°C

Grain size / μm	PC				C + 1000 W			
	Region			Average	Region			Average
	1	2	3		1	2	3	
1 h	5.48±0.06	5.17±0.08	6.24±0.05	5.63±0.61	6.65±0.05	5.73±0.05	6.73±0.05	6.37±0.064
3 hs	12.10±0.08	10.67±0.09	12.35±0.07	11.71±1.03	12.89±0.06	11.40±0.09	12.63±0.08	12.31±0.91
5 h3	16.33±0.08	15.41±0.07	16.68±0.06	16.41±0.73	18.44±0.07	15.88±0.07	16.45±0.08	16.92±1.04

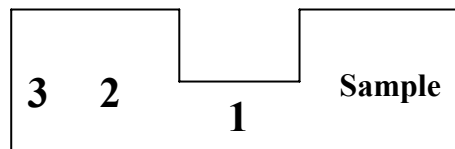


Table 4.11 shows the change of density ZnO before annealing and after annealing. An increase of density was observed at low annealing temperatures and then a decrease at high temperatures.

Table 4.11. Relative density of submicron ZnO pellets before annealing and after annealing at 900 °C, 1000 °C, 1050 °C, 1100 °C, 1150 °C and 1200 °C.

Relative density / %		Before annealing	PC	Δ	Before annealing	C + 1000 W	Δ
900°C	5 hs	98.4	98.9	0.5	98.5	98.8	0.3
1000°C	5 hs	98.7	98.7	0	98.9	99.2	0.3
1050°C	5 hs	98.7	98.7	0	98.8	98.8	0
1100°C	1 h	98.9	98.9	0	98.9	98.9	0
	3 hs	98.9	98.9	0	98.9	98.9	0
	5 hs	98.9	98.9	0	98.9	98.4	-0.5
1150°C	1 h	98.9	98.9	0	98.9	98.7	-0.2
	3 hs	98.9	98.4	-0.5	98.9	98.3	-0.6
	5 hs	98.9	98.2	-0.7	98.9	97.9	-1.0
1200°C	1 h	98.9	98.0	-0.9	98.9	98.3	-0.6
	3 hs	98.9	97.6	-1.3	98.9	97.9	-1.0
	5 hs	98.9	97.5	-1.9	98.9	98.3	-0.6

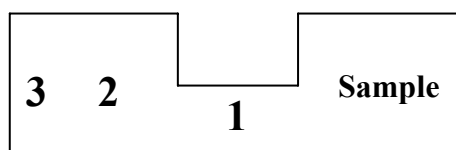
Table 4.12 shows the porosity of the ZnO pellets after having been annealed at 1100 °C and 1150 °C. It can be seen that fewer pores were formed in the edge region.

Table 4.12. Porosity of different parts in the ZnO pellets annealed at 1100 °C and 1150 °C. At 1100 °C.

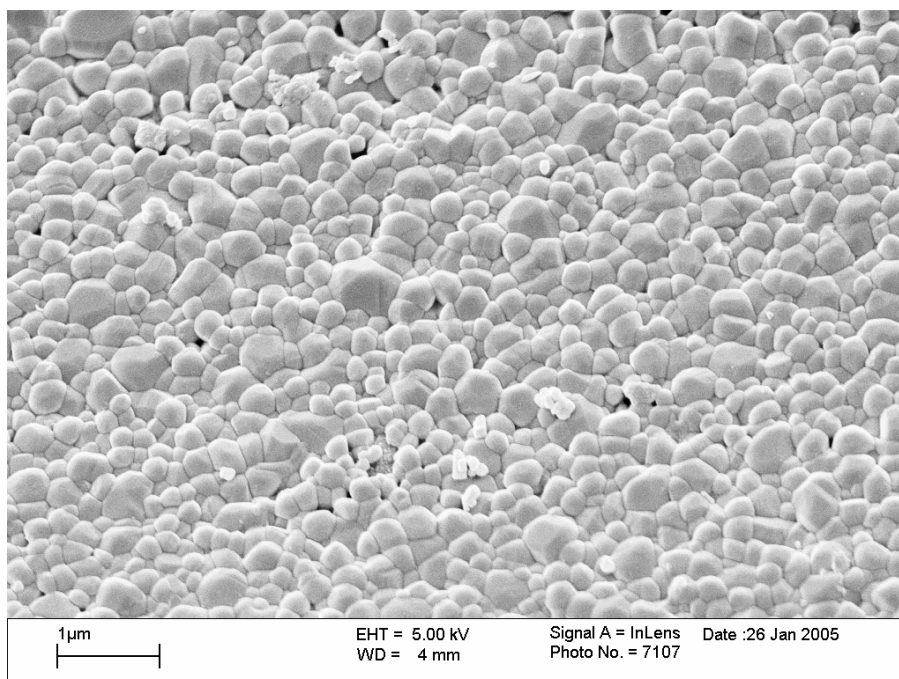
Porosity / %	PC			C + 1000 W		
	1	2	3	1	2	3
1h	1.2	1.3	0.6	1.3	1.4	0.6
3hs	1.5	1.6	0.9	1.8	1.9	0.9
5hs	1.6	1.7	0.9	1.7	2.0	1.0

At 1150 °C

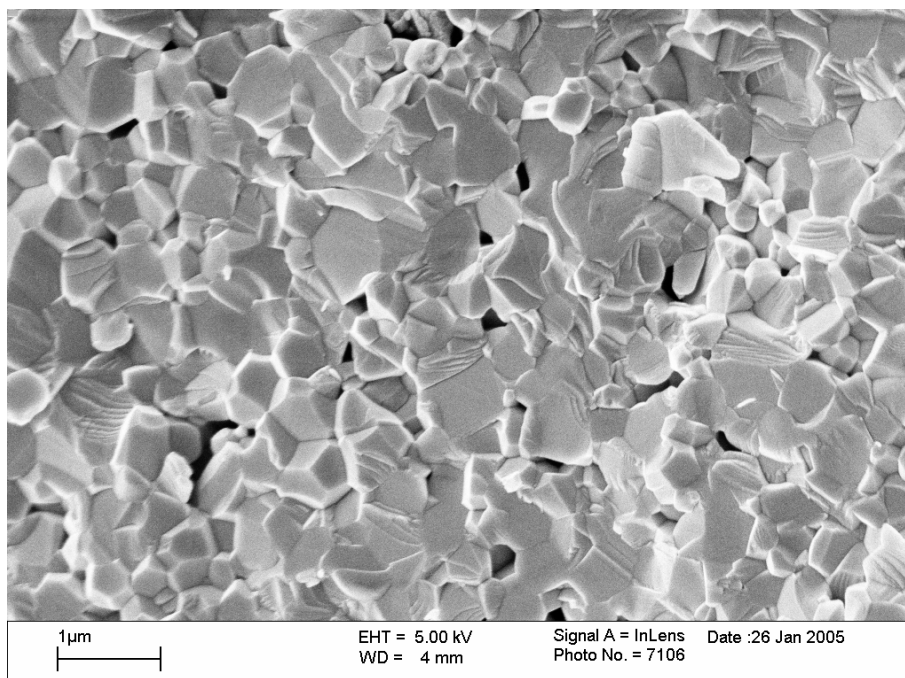
Porosity / %	PC			C + 1000 W		
	1	2	3	1	2	3
1h	1.3	1.4	0.6	1.3	1.8	0.9
3hs	1.6	1.7	0.6	1.7	1.9	0.8
5hs	1.7	1.8	0.5	2.4	2.8	0.7



The surface of the sample sintered by two step sintering always had smaller grain than the bulk centre as shown in figures 4.48 and 4.49.

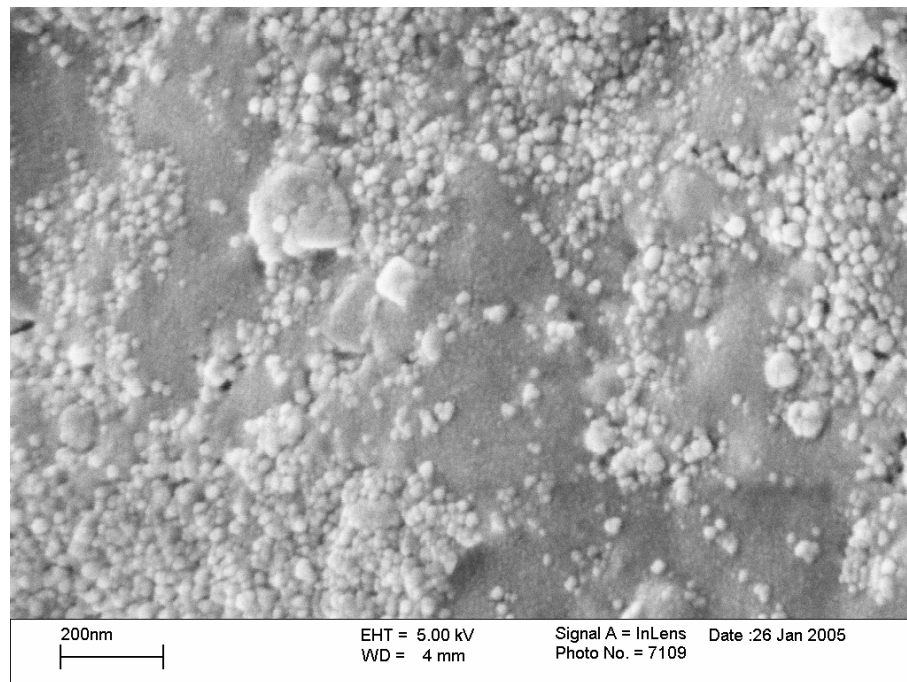


Surface

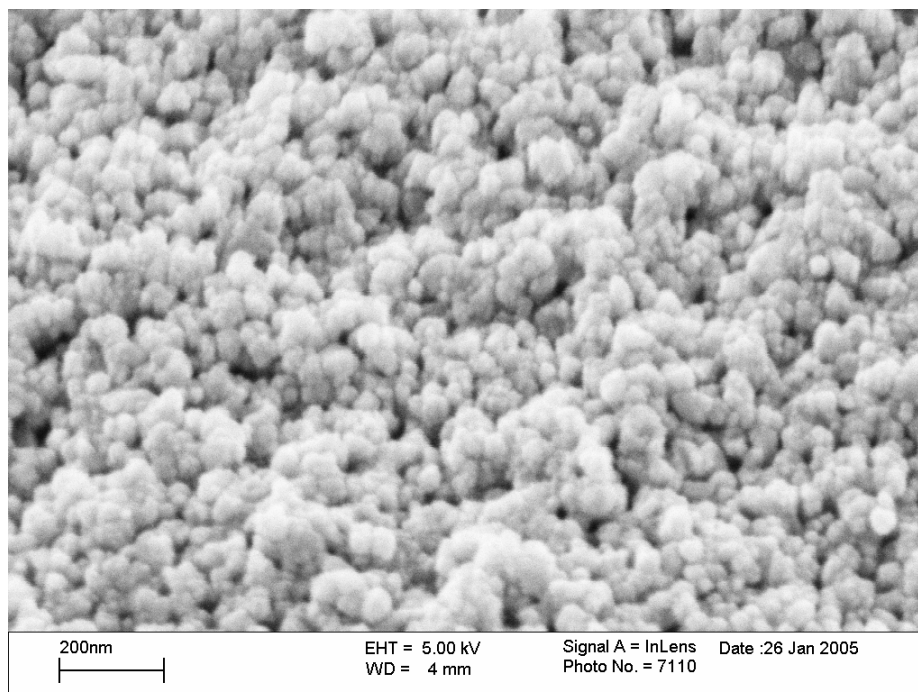


Centre

Figure 4.48. FEG-SEM micrographs of ZnO pellets before annealing after two step sintering.



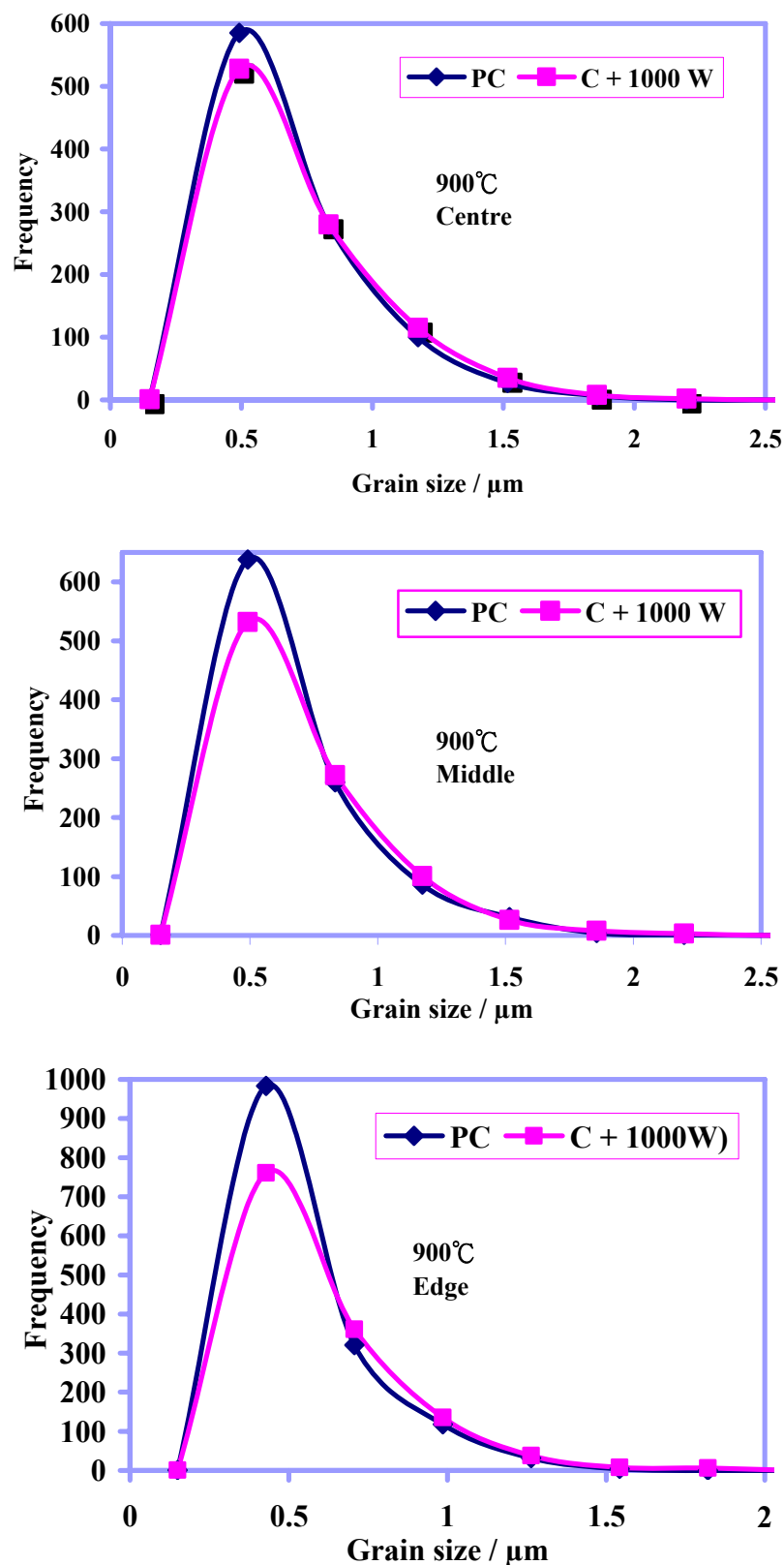
Surface



Centre

Figure 4.49. FEGSEM micrographs of nano 3-YSZ pellets after two step sintering.

Figure 4.50 shows the grain size distribution of different regions of the submicron ZnO pellets before annealing and after annealing at 900°C and 1000°C for 5 hours in pure conventional heating and hybrid heating with 1000 W microwave power. It can be noted that there was an overall increase in grain size with hybrid heating compared to conventional heating.



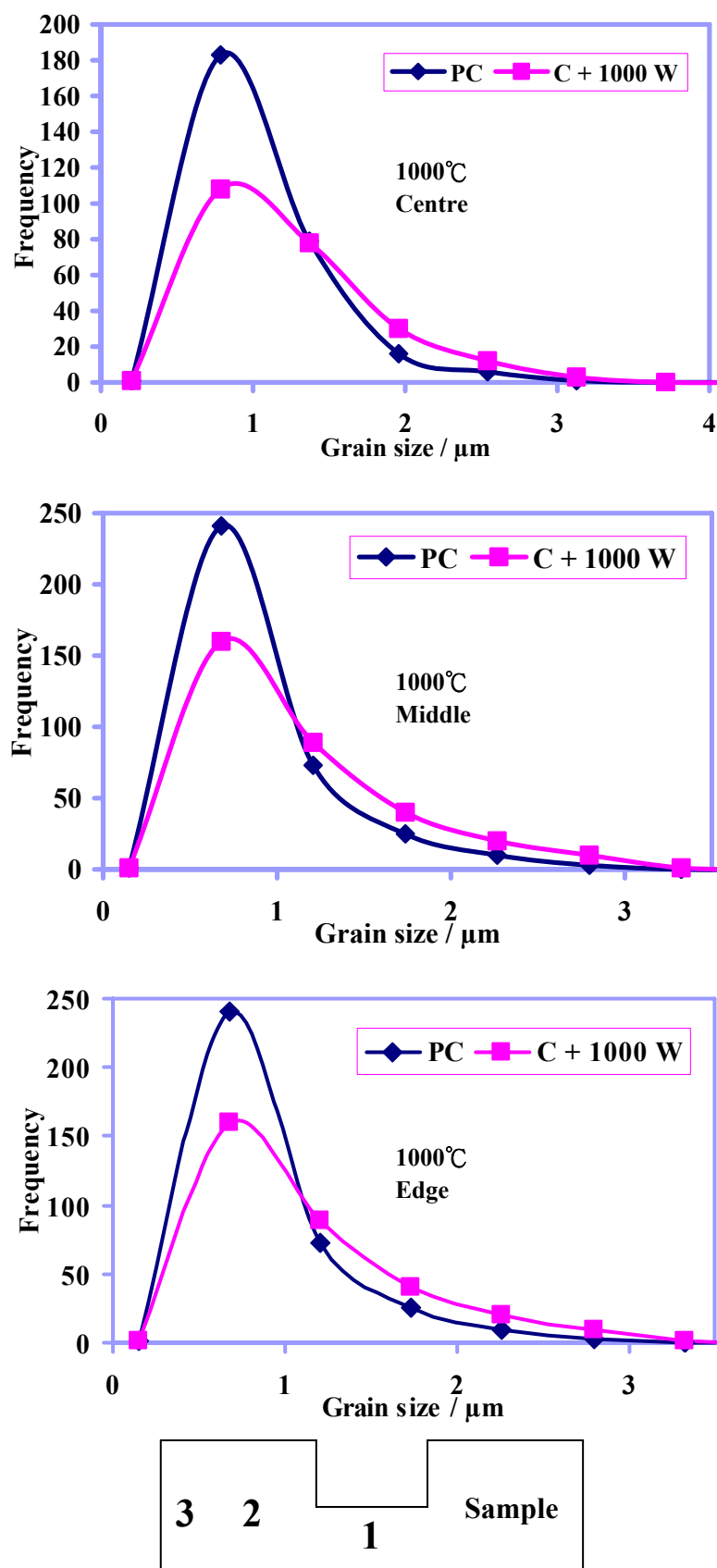
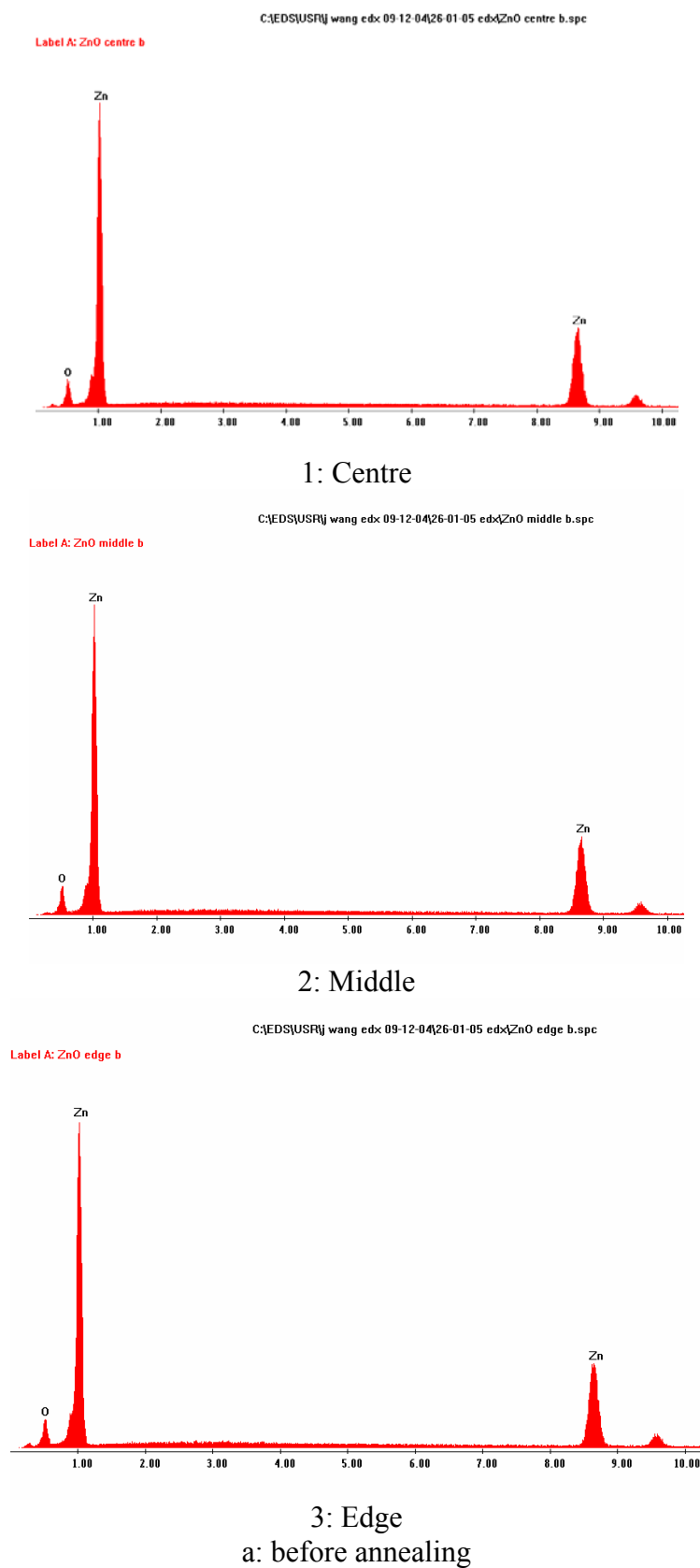
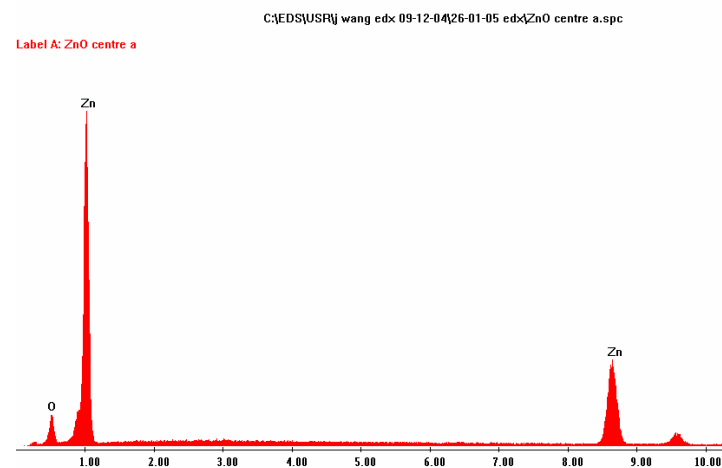


Figure 4.50. The grain size distribution of submicron ZnO pellets as a function of region before annealing and after annealing at 900 °C and 1000 °C for 5 hours in pure conventional heating and hybrid heating with 1000 W microwave power.

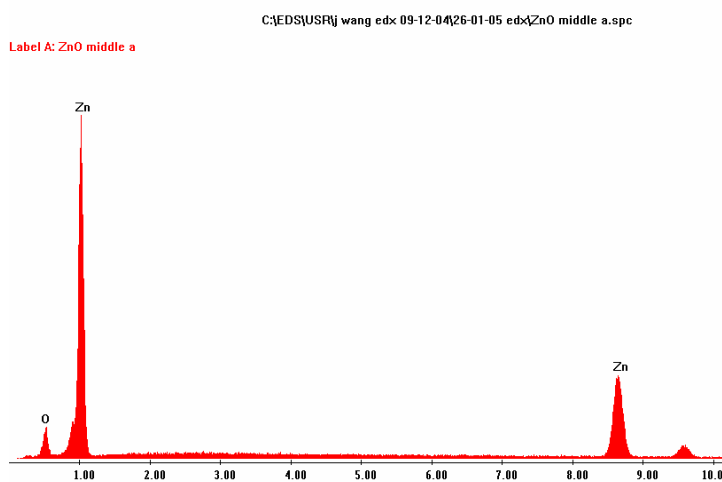
4.4.3. EDAX ANALYSIS

EDAX analysis showed that no other elements except zinc and oxygen were found before and after annealing the ZnO pellets, as shown in figure 4.51.

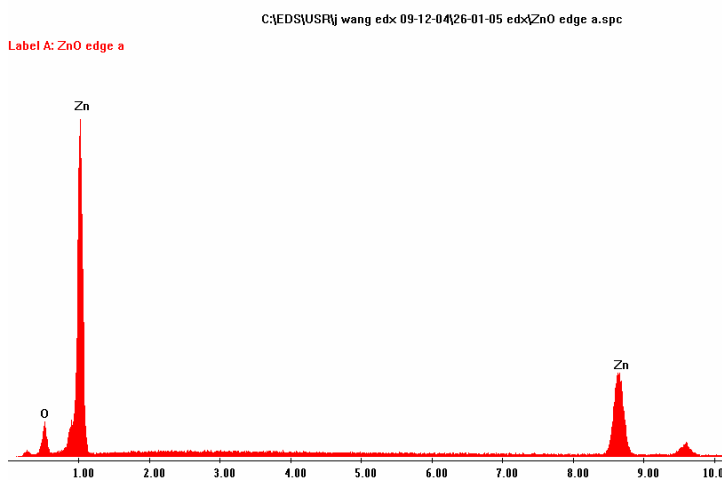




1: Centre



2: Middle



3: Edge
b: after annealing

Figure 4.51. EDAX spectra of ZnO pellets as a function of region before and after annealing.

4.4.4. GRAIN SIZES OF ANNEALED ZINC OXIDE AS A FUNCTION OF TEMPERATURE AND TIME

Figures 4.52 and 4.53 show the grain growth of ZnO pellets annealed during conventional and hybrid heating at different temperatures. Pronounced enhancement occurred at 1100°C and 1150°C during hybrid heating throughout the samples.

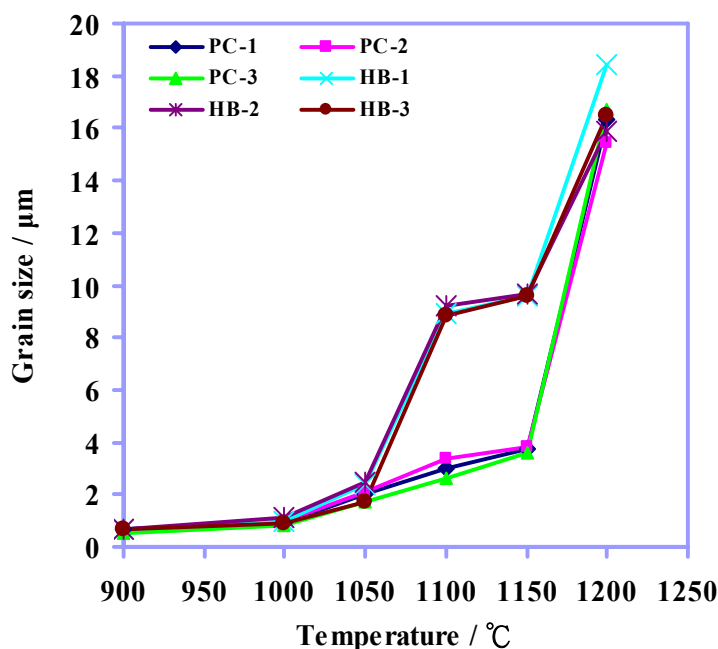


Figure 4.52. Average grain sizes of annealed ZnO samples as a function of temperature and region (1:centre, 2:middle and 3:edge) during pure conventional (PC) and hybrid heating (HB) with 1000 W microwave power ($C + 1000\text{ W Mw}$) for 5 hours.

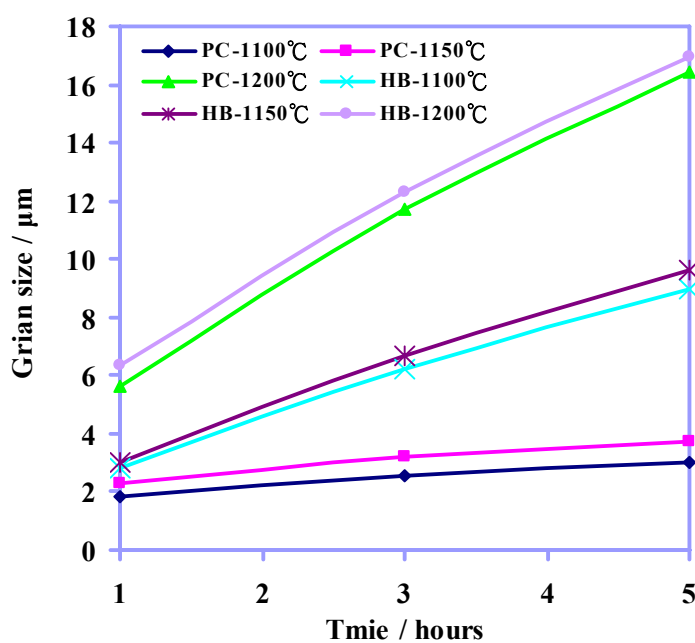


Figure 4.53. Average grain size of annealed ZnO samples as a function of time during pure conventional (PC) and hybrid heating (HB) with 1000 W microwave power at 1100 °C, 1150 °C and 1200 °C.

4.4.5. TEMPERATURE GRADIENTS DURING ANNEALING

Using two OFT probes as described in section 3.2.3, the temperature differences between body centre and edge of the annealed samples in pure conventional heating and hybrid heating with 1000 W microwave power at the start and end of annealing at 900°C, 1000°C, 1050°C, 1100°C, 1150°C and 1200°C for 5 hours were obtained as shown in table 4.13. The highest temperature difference was 19°C.

Table 4.13. Temperature differences of ZnO pellets annealed at different annealing temperatures ($\Delta T = T_s - T_c$)

Annealing temperature / °C	Starting ΔT / °C		End ΔT / °C	
	PC	C + 1000W	PC	C + 1000W
900	15	13	5	0
1000	16	14	4	0
1050	16	14	5	1
1100	16	13	3	1
1150	18	14	4	1
1200	19	14	4	1

T_s and T_c are body centre and surface temperatures, respectively.

Chapter 5

DISCUSSION

5.1 EVALUATION OF TEMPERATURE MEASUREMENT TECHNIQUES DURING MICROWAVE HEATING

5.1.1. MELTING POINT MEASUREMENT OF V_2O_5 IN MICROWAVE HEATING

From table 4.1, it can be seen that whilst the OFT provided very accurate results, neither the pyrometer nor the thermocouples did so. The error in the pyrometer is believed to be due to the width of the measured area being somewhat larger than the diameter of the hole drilled into the sample. Given the inverse temperature profile that occurs in microwave heated samples, this meant that an average value was obtained rather than the true value.

The very low values observed with the thermocouples was surprising and might be due to the insulating effect of the air gap between the thermocouple tip and the metal sheath and thermal conduction by the sheath. It is interesting to note that the larger thermocouple was less accurate, this would tend to support the above arguments. Piluso *et al* used a 1 mm diameter thermocouple to measure the melting point of the eutectic composition of 49.4 wt% CaO + 50.6 wt% Al_2O_3 , which melts at 1360°C and found a discrepancy of 40°C [141]. This indicates that even when a thermocouple

with a smaller diameter is used in microwave heating, a big temperature error still exists.

Figure 4.1 shows the influence of the level of microwave power on the accuracy of the temperature measurement for the 3 mm diameter thermocouple. It can be seen that the greater the used power, the less accurate the measurement. This is explained by the fact that the higher the power level the faster the heating rate and so the greater the lag arising due to the thermal conduction of the air gap between sheath and thermocouple tip. This further supports the above arguments.

5.1.2. THERMAL RUNAWAY

Thermal runaway was always observed when the temperature of the zinc oxide sample was greater than 400°C for the experiments involving pure microwave heating and temperature measurement by a 1.5 mm diameter type R thermocouple (1.5RT) touching the sample, as shown in figure 4.2. This suggested that the thermocouple was enhancing the local microwave field adjacent to the sample in the same manner as a lightning conductor [87]. Figure 4.3 shows how the V_2O_5 pellet only melted locally during microwave heating when the 1.5 mm diameter thermocouple was in contact with the sample, further revealing the enhanced local microwave field around the thermocouple tip. In contrast, no thermal runaway was observed for the 3 mm diameter thermocouple (3RT). This suggested that the smaller the size of the thermocouple, the greater the enhancement of the local microwave field.

It was also noted that thermal runaway could be caused in all the materials with the 1.5 mm thermocouple if the gap between sample and thermocouple was narrow enough and the temperature exceed a critical value, figures 4.4 and 4.5. Discharging was also detected through a quartz window on the cavity when thermal runaway occurred, this suggested that it was discharging that led to thermal runaway when there was a small gap between the sample and the thermocouple. This can be explained by the same reasoning used above – thermocouple focusing. This is because the latter will have caused a large, local electric field which gave rise to a very large voltage between the sample and thermocouple, causing discharging through the air as the air was ionised and broken down with increasing temperature [87, 142].

Further evidence of the field-focusing effect of thermocouples was obtained by Jaglin *et al* during the microwave heating of a SiC-based ceramic using a thermal imaging camera [140]. Figure 4.6 provides a digitally captured thermal image during the microwave heating of a porous SiC foam prior to undergoing chemical vapour infiltration (CVI). During the microwave assisted CVI process, an inverse temperature profile is deliberately created in order to preferentially deposit a ceramic matrix from the centre of a porous preform towards the surface in order to achieve maximum densification in the shortest time. However, when thermocouples were used for the temperature measurements, SiC deposition was always found to occur around the thermocouple tip, wherever it was located in or on the sample [140].

In general, the use of a thermocouple in microwave heating can significantly change the heating behaviour of the processed materials and even lead to the loss of microwave energy due to discharging.

5.1.3. PROBLEMS WITH THE USE OF OFTS FOR TEMPERATURE MEASUREMENT DURING CONVENTIONAL HEATING

Whilst the melting point measurement using V_2O_5 showed that an OFT could be very accurate for both microwave and conventional heating, a comparative study of a thermocouple and an optical fibre thermometer always registered a higher temperature in the low temperature range, as shown in figure 4.7, and that the lower the temperature, the bigger the difference between the temperatures measured by the thermocouple and the OFT. A possible explanation is that the radiation from elements affects or disturbs the temperature measurement of an optical fibre thermometer, as shown in figure 4.8. Similar claims were earlier reported by Grellinger and Janney *et al* [143]. During the melting point measurement using V_2O_5 , the OFT sensor was protected from the strong radiation by being buried in the V_2O_5 powder, as shown in figure 4.9.

In order to improve low temperature measurements with an OFT, a clay-based coated alumina tube was used to shield the OFT sensor; this worked satisfactorily if, the appropriate thickness of the coating was selected. Since the coating and alumina tube did not absorb microwaves they did not influence the microwave heating of the sample during the hybrid heating experiments.

5.2. SINTERING EXPERIMENTS

5.2.1. SINTERING

As has been seen in the literature review, one of the arguments on whether “the microwave effect” exists has been caused by the use of different thermal conditions or thermal histories during conventional and microwave heating. Therefore, it was necessary to allow all the samples to be sintered with the same thermal history in the present work.

From figures 4.14, 4.15 and 4.16, it can be seen that during the sintering experiments all the ZnO and 3-YSZ samples underwent identical temperature – time profiles irrespective of the amount of microwave power used, using the same experimental system. Similar curves were obtained for other samples sintered at different sintering temperatures. This means that the pellets from the same powder sintered at the same sintering temperature experienced the same thermal history. This allowed direct comparisons to be made.

During hybrid heating, it can be seen that as the level of microwave power was increased, there was a decrease in the amount of conventional power required to hold the desired sintering temperature, however, the decrease in conventional power is less than the increase in microwave power, figures 4.17 and 4.18. This strongly suggests that not all of the microwave power entering the applicator was being absorbed by the sample; a fact that is not too surprising. Figure 4.19 shows the same results for the sintering of the 3-YSZ samples, again it can be seen how less conventional power was required as the level of microwave power increased, but the changes were not proportional.

5.2.2. DENSIFICATION

5.2.2.1. DENSIFICATION OF PELLETS

5.2.2.1.1. Enhanced Densification and Factors to Affect Densification

Effect of microwave power and temperature

Figures 4.20 and 4.21 show the influence of the amount of microwave power on the resulting density of the pellets from the submicron- and micron-sized ZnO powders after sintering at 680°C, 780°C and 900°C, respectively, whilst figures 4.26, 4.27 and 4.28 show the same data for the pellets from the nano-sized and submicron-size 3-YSZ and submicron 10-YSZ powders sintered at 900°C, 1000 °C, 1100°C, 1200°C, 1220°C and 1260°C. In all cases it can be seen that there was a substantial increase in the degree of densification achieved as the microwave power level increased, with the greatest increase occurring at the lower sintering temperature used and with the pellets from the submicron-sized powers. The general trend achieved, of an increase in density with an increase in the fraction of microwave energy used, was also observed by Wroe *et. al.* [59]. A similar trend occurred not only in the bulk material but also in the film material such as sol-gel alumina films, as will be seen in a later section.

Additionally, all the observed materials displayed the greatest enhancement at intermediate sintering temperatures, with the effect decreasing with increasing densification, figure 4.22. The basic shape of the densification curve was the same for both conventional heating and hybrid heating, suggesting that the fundamental mechanism could be similar when microwaves are used.

There are two possible explanations for the enhancements observed during densification with hybrid heating:

- i) the microwaves cause a genuine effect, enhancing the sintering process;
- ii) the use of microwaves results in temperature gradients within the samples which accounts for the results observed.

Figure 4.21 shows the effect of the sample size on the results for the ZnO pellets from the submicron-sized powder at 680°C in which the largest ‘effect’ was seen. It can be seen that there is no difference for any of the samples except that measuring 25 mm in diameter by 5 mm in thickness. This result will be discussed later. Since it would be expected that sample size would affect the magnitude of any temperature gradients, this is preliminary evidence that any such gradients may not be significant, something which will be demonstrated further later in the thesis.

In the mean time, some factors that could have affected the densification enhancement during hybrid heating will be discussed.

Effect of dielectric losses, ionic conductivity and grain size

The density data from all the sintered materials with different loss factors and from different powders consisting of different size particles using pure conventional heating and hybrid heating with 1 kW microwave power are shown in table 5.1.

It can be seen that all the materials showed microwave enhancement in varying degrees and that the enhanced level changed with dielectric loss factor, ionic conductivity and grain sizes of materials as shown in tables 5.1 and 3.1.

The greatest degree of microwave enhancement was found in ZnO, the highest dielectric loss material observed. Increases of ~23 % and 18 % were observed in the submicron and micron ZnO samples respectively at 680°C and 780°C by using hybrid sintering with 1000 W microwave power compared to pure conventional sintering. In contrast, in the lowest dielectric loss material, alumina, very little microwave enhancement was obtained, just 2.4% increase for the sol-gel synthesised nano alumina pellets. The YSZ-based ceramics, which exhibit an intermediate loss, showed intermediate behaviours, suggesting that the increase in density with hybrid heating might depend largely on the dielectric loss of the materials. These results are in agreement with the study reported by Xie *et al* [9], in which three kinds of ceramics with different dielectric losses, Al₂O₃, Ce-Y-ZrO₂ and lead-based relaxor ferroelectrics (PMZNT) were sintered using 2.45 GHz microwave power and pure

conventional power. Bigger increases in densification were observed with microwave heating in the high dielectric loss Ce-Y-ZrO₂ and the high ionic conductive loss PMZNT compared to the lower loss Al₂O₃.

Table 5.1. Densities of sintered materials using pure conventional heating and hybrid heating with 1 kW microwave power.

Materials	Approach	Sintering temperature / °C	% Theor. density	Δ % Theor. density
Submicron ZnO Sigma-Aldrich	Conv. +1 kW Mw	680	91.5	23.3
	PC		68.2	
	Conv. +1 kW Mw	780	97.2	7.2
	PC		90.0	
Micron ZnO Sigma-Aldrich	Conv. +1 kW Mw	780	86.3	17.7
	PC		68.6	
	Conv. +1 kW Mw	900	92.6	8.6
	PC		84.0	
Submicron 3-YSZ HSY-3U	Conv. +1 kW Mw	1100	69.4	12.4
	PC		57.0	
	Conv. +1 kW Mw	1200	95.5	3.1
	PC		92.4	
Nano 3-YSZ MEL	Conv. +1 kW Mw	900	86.4	12.8
	PC		73.6	
	Conv. +1 kW Mw	1000	96.2	6.7
	PC		89.5	
Submicron 3-YSZ MEL	Conv. +1 kW Mw	1220	73.3	15.1
	PC		58.2	
	Conv. +1 kW Mw	1260	85.3	10.5
	PC		74.8	
Submicron 10-YSZ MEL	Conv. +1 kW Mw	1220	77.7	17.5
	PC		60.2	
	Conv. +1 kW Mw	1260	88.9	12.5
	PC		76.4	
sol-gel synthesised alumina	Conv. +1 kW Mw	1180	59.2	2.4
	PC		56.8	
	Conv. +1 kW Mw	1260	62.4	1.8
	PC		60.6	
Nano alumina Sigma-Aldrich	Conv. +1 kW Mw	1400	85.3	1.2
	PC		84.1	
Sigma-Aldrich Silica	Conv. +1 kW Mw	1000	77.6	15.3
	PC		61.3	

However, there have also been reports in the literature in which a significant apparent enhancement was observed when microwave sintering alumina. For example, Janney *et al* used 28 GHz microwaves to sinter doped alumina at ~250°C lower than conventional heating [144], similar results were also obtained using 2.45 GHz

microwaves by Brosnan *et al* [33]. Using high microwave powers, Xie *et al* and Samuels *et al* also observed much higher densification in alumina with high purity in microwave heating compared to conventional heating. Great care must be taken when considering these results, however, since they were typically obtained using separate microwave and conventional sintering furnaces with quite different specifications and often with different temperature measurement systems.

In the present work, it was also observed that when two materials with different ionic conductivity, e.g. submicron 10-YSZ and submicron 3-YSZ, were sintered using hybrid heating with the same microwave power, the submicron 10-YSZ, which has greater ionic conductivity, displayed better densification at the same sintering temperature than the submicron 3-YSZ and that the trend increased with increasing microwave power, as shown in figure 4.28. These results suggest that a higher ionic conductivity can contribute to higher densification and that the effect is enhanced by the presence of a microwave field. These results are in good agreement with those reported by Samuels *et al* [8] and Nightingale *et al* [116] and are also supported by the study reported by Janney *et al* [145], who found that zirconia doped with 12 mol% CeO₂ displayed a much lower microwave enhancement than 8-YSZ, which has a higher ionic conductivity than that of ceria-zirconia by a factor of ~100 [116]. These results are not surprising, since ionic conductivity in zirconias is related to the presence of oxygen vacancies in the lattice – a factor which also positively affects sintering.

Finally, the effect of powder particle size on the enhancement of densification was also observed as shown in figures 4.20, 4.26, 4.27 and table 5.1. For example, whilst a ~23% increase in density was achieved with the submicron ZnO samples at 680°C, a ~18% increase was observed in micron ZnO samples at 780°C. Comparison of the curves in figures 4.20 (a) and 4.20 (b) suggests that similar degrees of densification are occurring at these two temperatures for the two different grain size ceramics. Similar results were also found for the 3-YSZ and alumina samples; the general trend is that the finer the grain size of the starting powder, the higher the microwave enhancement and that this size effect is stronger at the early stages of sintering; a not too surprising result.

Compared to alumina, silica with the similar loss factor showed a greater microwave enhancement during hybrid heating than alumina. A 15% increase in density of silica was obtained during hybrid heating with 1000 W microwave power compared to pure conventional heating. The reason to cause it is not clear, hence, further work needs to be done to explain it, including the examination of physical and chemical properties for this silica material.

5.2.2.1.2. Microstructure Observation

In each case, microstructures show significantly greater densification and a larger average grain size in the hybrid heated samples as shown in Figures 4.23, 4.24, 4.25 and 4.29, supporting the evidence as shown in figures 4.20, 4.21 and 4.26.

Figures 4.23 and 4.24 are both fracture surfaces from the sintered ZnO pellets made from the submicron-sized powder, in the former the temperature at the surface centre of the sample was controlled whilst in the later it was the temperature at the centre. The change to the centre was adopted part-way through the experimental work to allow ease of comparison with other work, but as was observed, there was negligible effect on the resulting microstructures.

5.2.2.1.3. Grain Growth in Sintering

Through the X-ray diffraction pattern for ZnO ceramics sintered at 680°C and ZnO powder as shown in figure 4.33, grain sizes were calculated by equation 3.2 and are shown in figure 4.34. It is noted that the grain growth was also sensitive to the microwave power; and that with increasing microwave power, the grain size increased. Figure 4.34 reveals that the enhanced densification was accompanied by a rapid increase in grain size with increased microwave power. This means that the microwaves not only enhanced densification but also grain growth. Table 4.7 shows the result of grain sizes by FEG-SEM examination. Compared to the results estimated

by XRD, the grain sizes were smaller. This indicates that in calculating grain size by Scherrer equation, β should be calibrated. But the measurement accuracy did not disturb the comparison between materials with the same component. The results obtained by FEG-SEM also show that the grain sizes in the samples sintered by hybrid power were larger than those in the samples sintered by pure conventional power, further supporting the above results.

5.2.2.1.4. Observation Using a Dilatometer

It can be seen that no thermal runaway occurred during the whole sintering process using hybrid heating, and that the final densities of ZnO pellets measured by the Archimedes method were consistent with those estimated by the dilatometer. As indicated by figure 4.35, the densification in hybrid heating started earlier than that in pure conventional heating and progressed faster.

5.2.2.2. ENHANCED MICROWAVE SINTERING: POSSIBLE EXPLANATIONS

The results obtained to date suggest that there is indeed a microwave effect observed during the sintering of ceramic materials that takes the form of enhanced sintering, i.e. greater densification at a given temperature compared to conventional sintering. It also appears that the size of the effect increases with increasing microwave power, i.e. greater microwave field, although the shape of the curve is not linear, rather the greatest effect occurs at intermediate power levels. This same trend seems to be true for different materials, though only four have been examined to date, and to increase in magnitude for finer precursor powders. Sample size generally seems to have little or no effect – provided it remains below some critical size. If the sample is above the critical size then, when the amount of microwave power used is high, the degree of densification increases sharply and it becomes increasingly difficult to control the temperature during sintering, both of which are generally regarded as being indicative of thermal runaway. Whilst it could be argued that the microstructures shown in figure 4.39 support this conclusion, experimental measurements have failed to detect

any significant temperature gradients across the body to date. Whilst further work is clearly needed to resolve this issue, a number of possible explanations are being considered, including:

5.2.2.2.1. Local Temperature Gradients

Figure 4.37 shows the temperature-time profile for a ZnO sample measuring 25 mm diameter by 5 mm thick sintered at 680°C for one hour using 600 W of microwave power. These are the samples that repeatedly showed excessive densification when sintered using ≥ 600 W of microwave power. Close examination reveals that there is a small ‘blip’ in the central (i.e. control) temperature near the end of the one hour hold. This is when the temperature monitored by the central OFT probe started to increase rapidly. To compensate, the conventional power was immediately decreased, with the result that the edge temperature decreased sharply. This result generally supports the idea that thermal runaway is occurring toward the end of the hold period. However, on its own, this could not account for the increased density since, as figure 4.37 shows, the temperature apparently does not increase beyond about 690°C at any point in the sintering run.

Figure 5.1 below shows the experimental temperature measurement configuration, one OFT probe measuring the central temperature whilst another measures the edge temperature. It is possible that in the larger samples a locally higher temperature could exist in a doughnut-shaped ring around the points marked X, i.e. intermediate between the two probes. If this gradient were sharp enough then it would result in a higher overall density being observed but without a high temperature being registered by the probes. Experimental evidence for such a ring-shaped inverse temperature profile has been observed before during the microwave reaction bonding of silicon nitride when the samples were larger than the depth of penetration of microwaves into the precursor silicon compact [146].

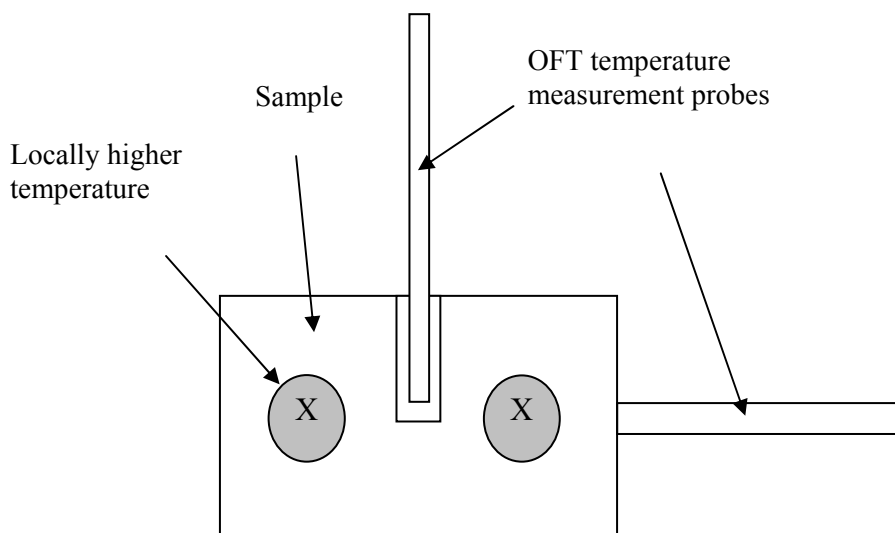


Figure 5.1. A schematic diagram of possible location of a higher temperature profile in large ZnO samples [146].

To determine whether this is indeed occurring, a number of experiments will need to be performed. These include:

- The use of a third OFT probe located in the critical area, though the need to drill an additional hole in the sample could affect the results;
- Dicing the sintered sample to see if local variations in density can be observed and whether they form the pattern suggested in figure 5.1.

However, the fact that size has no apparent effect for the smaller samples suggests that without the onset of thermal runaway, large temperature gradients do not exist and therefore are unlikely to account for the relatively large increases in density observed with increasing microwave power. Therefore other explanations need to be found and temperature distribution profiles in the samples need to be obtained via other techniques such as the use of a thermal image camera. This will be discussed further in section 5.2.3.

5.2.2.2.2. Change in Activation Energy

Figure 4.13 shows the density curve for submicron ZnO sintered conventionally. Comparison with the results in figures 4.20, 4.21 and 4.22 for the hybrid sintered

ceramic indicates that enhanced densification is most evident at temperatures corresponding to the range 650 – 800°C for conventional sintering and hence densification is enhanced primarily in the intermediate stage of sintering.

In this stage, for grain boundary diffusion, the rate of densification can be expressed by equation 2.44 [71]

$$\frac{1}{\rho} \frac{d\rho}{dt} \approx \frac{4}{3} \times \frac{D_{gb} \delta_{gb} \gamma_{sv} \Omega}{G^4 k T \rho (1 - \rho)^{\frac{1}{2}}}$$

and

$$D_{gb} = D_0 \exp\left(\frac{-\Delta E}{RT}\right) \quad (5.1)$$

where ρ is the density of the material, Ω is the atomic volume, γ_{sv} is the surface energy of the solid /vapour interface, δ_{gb} is the width of the grain boundary, D_{gb} is the diffusion coefficient for atomic motion across the grain boundary, k is Boltzmann's constant, G is grain size, ΔE is the diffusion activation energy, R is gas constant and T is temperature. It is evident from these equations that densification rate will increase when D_0 increases or activation energy decreases. So the cause of the accelerated densification in hybrid sintering might be the decrease of diffusion activation energy or a increase in the pre-exponential factor D_0 .

Janney et al, [127, 132] has performed a whole series of comparative experiments involving microwave and conventional heating of alumina ceramics. They report activation energies of 160 kJ/mol and 575 kJ/mol for pure microwave (28 GHz) and pure conventional sintering; of 480 kJ/mol and 590kJ/mol for grain growth using microwave and conventional annealing; and of 410 kJ/mol and 710 kJ/mol for O^{18} tracer diffusion in alumina using microwave and conventional heating, respectively. They argue that the different changes in activation energy observed is indicative of the different processes involved in each of the three experiments. During the sintering experiments for example, they observed differences both in the structural evolution and the kinetics of the processes. This, they concluded, meant that microwave and conventional sintering were two distinctly different processes with different activation energies [127, 132].

Conversely, the approximate similarity in effect for the grain growth and O^{18} tracer diffusion experiments suggested to them that the structural processes were essentially the same for microwave and conventional annealing [127, 132].

However, there was some confusion between the use of natural and base 10 logarithms and also in what constitutes the pre-exponential factor, i.e. whether it is D_0 or the logarithm of D_0 in the equivalent of equation 5.1 in Janney's paper [127]. This led to the conclusion that the pre-exponential factors were similar and hence it was assumed that the activation energies must be different. However, work in the TiC system [104] has suggested that it is more likely to be the pre-exponential factor that changes with little or no change in the activation energy. The pre-exponential factor is dependent on the vibration frequency of the atoms at the reaction interface and hence it could be postulated that this might be being affected by the microwave field though as yet there is insufficient evidence to draw firm conclusions from the present work.

5.2.2.2.3. Ponderomotive Force

Two independent investigations have sought to overcome the primary inherent difficulty associated with comparing microwave processing with conventional techniques, viz. the inability to vary the energy source without simultaneously affecting a wide range of other variables [59, 127, 132]. Both research groups have attempted to utilise hybrid microwave-conventional heating systems to perform their experiments enabling direct comparisons to be achieved, as in the present work. In the USA, Freeman *et al* [84] published the results of conductivity measurements made on sodium chloride single crystals under microwave and non-microwave conditions. Their results indicated that it was the driving force for diffusion that was enhanced by the application of microwaves rather than the vacancy mobility, which they found to remain unaffected. Similar conclusions were drawn by Wroe and Rowley [59] in the UK based on the sintering of partially stabilised zirconia. They found that an enhancement in densification when using microwaves was consistent with a dependence on the electric field experienced by the material. This suggested that the microwave field was inducing an additional (electric) driving force. Both these experimental results support the ponderomotive theory first suggested by Rybakov and Semenov in Russia [125, 131], see sections 2.2.3 and 2.2.4.

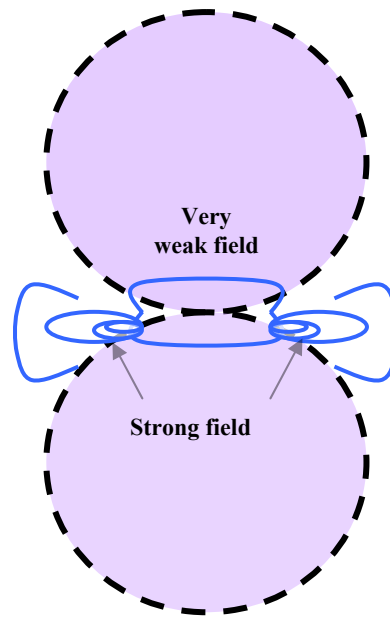


Figure 5.2. A schematic diagram of electric field focusing in the neighbourhood of two spherical ceramic particles [147].

Previous studies by Birnboim *et al.* [147] showed the very strong influence of the ceramic particle-to-particle and grain boundary geometry and properties on the overall permittivity. This suggests that the local electric fields can be disproportionately strong in certain regions such as interparticle contact zones, pores, and rough grain surfaces. For the two touching spheres model, the internal peak field in the neck region can be much larger than the average field in the material, up to 10 times that of the externally applied field, figure 5.2. The field in the neck region can be even higher, up to 30 times larger than the applied field. The net result is that the local absorbed energy in this region can be some 500 times larger than the average absorbed energy [147]. The experimental results to date certainly fit this theory well. Figures 4.20, 4.21, 4.22, 4.26, 4.27 and 4.28 showed that the most pronounced effect occurred during the intermediate stage of sintering, which is when the neck region dominates densification, whilst figures 4.20, 4.26 and 4.27 and table 5.1 demonstrate clearly the effect of particle size on the magnitude of the effect. As predicted by the ponderomotive theory, finer particles, which will have smaller and more neck regions, show an enhanced microwave effect compared to larger particles.

Additionally, by using the same two touching spheres model, Birnboim *et al* [147] carried out a comparative study of alumina and zinc oxide and found that the ratio of the internal or external peak field and the applied field for zinc oxide was larger than that for alumina as shown in table 5.2, further supporting the above results.

Table 5.2. Parameters of the total electric field integrated over all directions of the source [147].

Material	Peak internal/ applied field	Peak external/ applied field	Peak internal/ average internal
ZnO	6.9	22.1	333
Al ₂ O ₃	3.9	10.2	40

Clearly, considerable further work is required to determine precisely which mechanism is occurring during the microwave sintering of ceramic materials.

5.2.2.3. DENSIFICATION OF SOL-GEL ALUMINA FILMS

As has been seen in the above sections and the literature review chapter, it is important to avoid the occurrence of significant temperature gradients during the experimental observation of the “microwave effect”. Possible approaches include the use of controlling temperature via the centre temperature, as seen in the above sections and physically small samples such as ceramic films. Bykov, et al [36] reported a comparative study of pore evolution in nanostructured alumina membranes during annealing in a 10 kW, 30 GHz gyrotron microwave system and a conventional furnace; the results showed clearly that the enhancement of mass transport was found in the microwave case. However, in their study, because the precursor Al₂O₃ membrane was amorphous and low annealing temperatures were used, only γ -Al₂O₃ crystalline phase was formed and the grains were difficult to detect. Therefore, it was difficult to obtain significant information from this annealing process.

In the present work, sol gel Al₂O₃ films were annealed in the hybrid furnace to investigate their densification under conventional heating and hybrid heating. Examination by XRD showed that before annealing, the crystalline phase of the samples was γ -phase, whereas after annealing, they were α -phase, as shown in figure 4.32.

Figures 4.12g and 4.31 shows that the surface microstructures of the as-received and annealed films. It can be seen that in the samples annealed under identical time / temperature conditions at temperature 1160°C, no obvious differences were observed between the hybrid heated sample using 600 W microwave power and that annealed using conventional heating. However, a quite different microstructure was found in the samples annealed by hybrid heating with 1 kW microwave power, it can be clearly seen that the grain size and pore size were much larger. When the annealing temperature was 1200°C, it can be seen that grain sizes increased and densification tended to be higher with increasing microwave power.

Figure 4.30 shows the porosity curves of alumina films annealed at the two temperatures as the function of microwave power. It can be seen that with increasing microwave power, the porosity decreased. This suggests strongly that the microwaves enhanced the densification of the sol gel alumina films, in good agreement with the results obtained by Bykov *et al* [36], though a different starting material and different microwave frequency were used.

Effect on densification mechanisms

The driving force for the densification of a powder compact comes from the curvature difference between the particle surface and that of the neck. The initial stage involves rearrangement and agglomeration of particles, especially for fine particles, due to higher surface static charges (space charges) which may be adequate to rotate grains or clusters of grains into contact [148-151], and initial neck formation at the contact point between particles. The rearrangement consists of slight movement or rotation of adjacent particles to increase the number of points of contact. Bonding occurs at the points of contact where material transport can occur and where the surface energy is highest. All these can happen once heat is applied, the grains will lower their surface energy by the rearrangement and agglomeration of grains, immediately followed by the shrinkage of pores formed by the agglomeration of grains [148,151,152], forming large and irregular pores between the shrinking clusters of grains as shown in figure 4.31c. The process of densification caused by the rearrangement of grains will come to end as grains grow so large that the rearrangement movement of grains becomes more and more difficult. Surface diffusion, grain boundary diffusion and lattice diffusion dominate in the later sintering stages.

It has been demonstrated that microwaves enhanced densification of sol gel alumina films not only in the initial stage but also in the later stage. During the initial stage, one possible explanation for enhanced densification is that the interaction of microwaves with dielectric materials can cause net polarization in materials and that the interaction of the electric field component of the wave with charged particles in the materials accelerates the movement of charged particles and that more importantly, the microwaves lower the random thermal movement and make the alignment of particles become more regular. All these are beneficial for the rearrangement of particles and decrease the activation energy for the rearrangement of particles. Additionally, another reason that could lead to enhanced densification during the process of annealing of sol gel alumina films is that microwaves provide additional driving force for mass transport as reported by Bykov *et al* [60,131], as discussed in the above sections. They suggest that the steady-state vacancy flows resulting from the pondermotive effect can contribute to the densification of annealed materials. The large fraction of interface regions in the nanocrystalline materials, more space charges on grain boundaries and smaller pores and grains made this pondermotive effect more pronounced compared to microcrystalline materials.

5.2.3. TEMPERATURE GRADIENTS

5.2.3.1. USING TWO OPTICAL FIBRE THERMOMETERS

As has been discussed in the above sections, whether the microwave effect exists depends on whether there is a temperature gradient that is big enough to cause the observed increases during microwave hybrid heating. Although the preliminary evidence from sintering of a range of materials with different sizes has suggested that there were no large temperature gradients, more evidence was required.

As indicated in the experimental, temperature gradients were measured via the measurement of edge temperature and central temperature during hybrid heating. In addition, thermal image technique and further microstructure observation on the cross sections of samples were used to validate the results.

Figure 4.36 and table 4.8 show the temperature – time profiles and temperature gradients for submicron ZnO pellets measuring 13 mm in diameter by 5 mm in thickness sintered at 680°C using different microwave power levels. Several features may be observed.

- i) In every case, the temperature gradients were less than 10°C at any point in the sintering process.
- ii) Whilst the temperature gradient between the centre and edge was fairly consistent at $\sim 8 \pm 2^\circ\text{C}$ at the beginning of the sintering hold, it decreased towards the end of the 1 hour hold period; becoming very slightly inverted for the higher microwave power levels.
- iii) The average temperature of the samples was actually higher, the lower the level of microwave energy used, supporting the idea that the enhancement in densification as seen in figures 4.20 and 4.21 did not arise due to temperature gradients.

Figure 4.37 showed an interesting, and unusual, result. Whilst the densities of the submicron ZnO samples were generally unaffected by sample size, as shown in figure 4.21b the 25 mm diameter sample showed a significant increase in density when 600 W of microwave power was used. This result was repeatable and no results could be obtained when 800 and 1000 W of powers were used due to severe problems with thermal runaway.

Additionally, temperature gradients were further observed through examination of microstructures of ZnO pellets sintered in hybrid heating. Figures 4.38 and 4.39 are microstructure obtained from polished samples of the submicron ZnO pellets sintered at 680°C. Figure 4.38 shows that for a 13 mm in diameter by 5 mm thick pellet sintered using 800 W of microwave power the microstructures are very similar across the whole sample. In figure 4.39, the 25 mm diameter sample sintered using just 600

W of microwave power shows evidence of significantly larger grains in the centre and middle regions compared to the edge. This suggests very strongly that the centre of the sample has been somewhat hotter than the edge, a fact not borne out by the temperature gradient measurements, as shown figure 4.37. This will be discussed further in section 5.2.3.3. below.

Using the same method, the measured temperature differences between the edges and centres of YSZ, alumina and silica samples were all less than 25°C as shown in table 4.9.

5.2.3.2. THERMAL IMAGING

The surface temperature distribution was obtained through the use of a thermal imaging camera focused on the sample surface. Figure 4.4 shows the thermal images of the surface of 13 mm diameter ZnO pellets in pure conventional heating and hybrid heating with 1000 W microwave power and the resulting temperature distributions were plotted in figure 4.41. It can be seen that the samples sintered by hybrid heating always displayed slightly lower average surface temperatures and a smaller gradient than those sintered by pure conventional heating. Similar results were reported by Sorrell *et al* in microwave hybrid heating and pure conventional heating of hydroxyapatite and silicon carbide [41].

Whilst the 13 mm diameter ZnO pellets showed the development of a small inverse temperature profile towards the end of sintering in hybrid heating, the 25 mm diameter ZnO pellets displayed a quite different temperature profile, viz. a hotter ring between the centre and edge, figure 4.42. This means that the sample centre used temperature measurement, was not the hottest region. Hence, the real sample temperature and temperature gradients will have been underestimated. This provides a simple explanation of the achievement of higher density in the 25 mm diameter sample in figure 4.21b.

As indicated earlier, close examination of figure 4.20a suggested that a similar degree of densification occurred at 680°C with 1 kW mw power during hybrid heating (91.5%) and for pure conventional at 780°C (90%) for the submicron ZnO. This suggests that the effect of the microwaves is to enhance densification by approximately 100°C. A similar result may be observed for the micron ZnO in figure 4.20b and for the YSZ in figures 4.26 and 4.27; though here the effect is somewhat less than 100°C in line with its lower dielectric loss. Nevertheless, the apparent increases in densification observed are all significantly larger than could be accounted for by any temperature gradients reported. Additionally, the hybrid heated samples always displayed a slightly lower average surface temperature than those sintered conventionally, strongly suggesting that the microwave effect is genuine.

5.3. GRAIN GROWTH DURING ANNEALING OF ZINC OXIDE.

All the grain growth experiments were conducted using ZnO pellets sintered by the two-stage sintering technique [137]. The purpose of using this technique was to retain a fine grain size whilst achieving full densification so that grain growth could be observed easily. After two stage sintering, a relative density of >98% was achieved in all sintered samples and SEM examination showed that the average grain size was less than 0.5 μm , as shown in figure 4.44.

Figure 4.43 showed that during the annealing experiments all the samples experienced the same thermal history for any given annealing temperatures, as for the sintering experiments.

5.3.1. MICROSTRUCTURES AND GRAIN SIZE DISTRIBUTION

(1) Effect of annealing temperature and time on grain growth with and without microwaves.

Figures 4.44 and 4.45, table 4.10 and figure 4.52 illustrate the effect of annealing temperature on the grain growth of submicron ZnO using pure conventional and hybrid heating with 1 kW of microwave energy. It can be seen that whilst the use of microwaves enhanced grain growth at all temperatures, the greatest effect was in the intermediate range, as for the sintering studies. At 1100 and 1150°C there was a ~200% increase in observed grain growth during hybrid annealing for 5 hours compared to conventional heating. Additionally, it can also be seen that the increase in the grain growth with the use of microwaves increased with increasing annealing time at 1100 and 1150°C as shown in figure 4.53. All the results suggested that in the temperature range of 1100°C to 1150°C, grain growth was significantly influenced by the microwaves.

(2) Density and porosity

Table 4.11 shows that the annealed samples underwent slight changes in density during annealing. At low temperatures there was a negligible (~1%) increase in density whilst at higher temperatures the density actually decreased slightly. Similar results were reported by many authors in both pure ZnO and doped-ZnO ceramics [151, 153-162]. This is believed to be due to the breakdown of the ZnO and sublimation of atoms from the surface. Interestingly, however, as shown by table 4.12, the lowest porosity regions were at the surface of the samples. This suggests that there has been substantial diffusion of Zn ions from the middle to the surface, leaving vacancies in the lattice at the middle region and centre of the sample and hence resulting in porosity development.

One note of caution that must be emphasised here is that, for reasons that are currently unknown, the largest grains were not at the surface of the as-two stage sintered samples but in the centre as shown in figures 4.46 and 4.48. Given that the two-stage sintering was performed using conventional sintering, this is very difficult to explain, although the same result was also found in nano 3-YSZ sintered by two-stage

sintering as shown in figure 4.49. Further work is underway in the group at Loughborough to investigate this phenomenon.

(3) Evolution of grain size distributions during annealing.

A comparative study of grain size distribution under microwave and conventional conditions was conducted to indicate whether the evolution of grain growth that occurred during annealing was the same for both approaches. Figure 4.50 shows the grain size distribution of different parts of ZnO pellets annealed at 900 and 1000°C. It can be seen that for the pellets annealed with hybrid heating, there was a reduction in the number of fine grains and an increase in the larger grains compared to those annealed with pure conventional heating, and hence a larger average grain size. EDAX analysis showed that during the annealing process, no other elements except zinc and oxygen were found in the annealed samples as shown in figure 4.51. This means that no dopant contributed to the enhancement of grain growth.

5.3.2. GRAIN GROWTH KINETICS

As has been shown in the literature review chapter, the kinetic grain growth equation can be expressed by equation 2.61 [71, 153-165]

$$G^n - G_0^n = Kt$$

where n is an integer that depends on the diffusion mechanisms, impurity drag, pore drags and materials. Whereas K can be expressed by the Arrhenius equation:

$$K = K_0 \exp\left(-\frac{Q}{RT}\right) \quad (5.2)$$

where K_0 is the pre-exponential constant of the material, Q is the activation energy, R is the gas constant and T is the absolute temperature. Hence, the kinetic grain growth equation can be written to

$$G^n - G_0^n = K_0 t \exp\left(-\frac{Q}{RT}\right) \quad (5.3)$$

In this expression the initial grain size G_0 can be neglected because it is significantly smaller than the grain size G at time t . Thus, equation 2.61 and equation 5.3 can be simplified to

$$G^n = Kt \quad (5.4)$$

and

$$G^n = K_0 t \exp\left(-\frac{Q}{RT}\right) \quad (5.5)$$

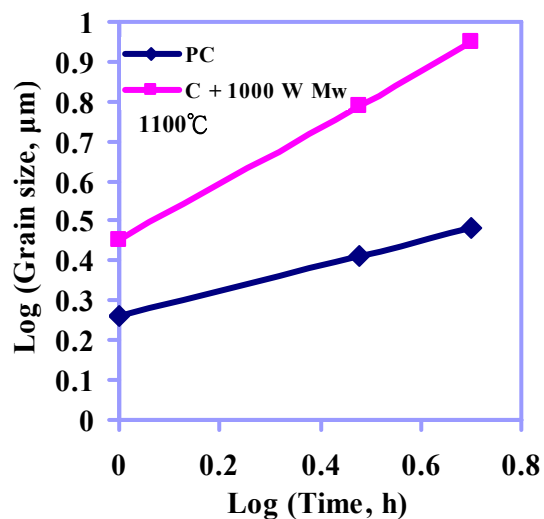
Equations 5.4 has been widely applied by many researchers to calculate the grain growth exponent value n [153-165].

The kinetic grain growth equation 5.4 can be plotted in the form:

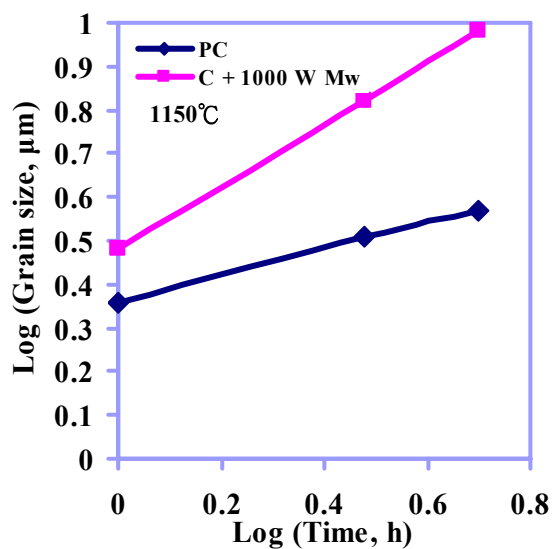
$$\log G = \frac{1}{n} \log K + \frac{1}{n} \log t \quad (5.6)$$

From the slope of the $\log G$ versus $\log t$ line, which is $1/n$, the grain growth exponent value n can be determined. Figure 5.3 illustrates the grain growth results of ZnO annealed at 1100°C and 1150°C during pure conventional heating and hybrid heating with 1000 W microwave power whilst table 5.3 shows the ‘ n ’ values of ZnO. They were 3.3 during pure conventional heating and 1.4 during hybrid heating with 1000 W microwave power, respectively.

Many researchers have reported the grain growth results of undoped ZnO in pure conventional heating and the grain growth exponent value, n , obtained by them is about 3 in the same temperature range [153-164], showing good agreement with the present results. The ‘ n ’ value for hybrid heating with 1000 W microwave power was reduced to 1.4, indicating the grain growth rate of ZnO annealed in hybrid heating was greater than that in pure conventional heating in the range of 1100°C to 1150°C.



a



b

Figure 5.3. Grain growth of ZnO pellets annealed at 1100 °C and 1150 °C.

Table 5.3. Grain growth exponent values for un-doped submicron ZnO at 1100 °C and 1150 °C during pure conventional heating and hybrid heating

Approach	n values at 1100 °C	n values at 1150 °C
PC	3.3±0.1	3.3±0.1
C + 1000 W Mw	1.4±0.1	1.4±0.1

5.3.3. MECHANISM OF ENHANCED GRAIN GROWTH

The temperature gradients during annealing were obtained by measuring the temperature difference between body centre and edge in pure conventional heating and hybrid heating with 1000 W microwave power at the start and end of annealing. Table 4.13 shows that the maximum temperature difference appeared at 1200°C in pure conventional heating, which was 20°C. Figure 4.53 indicates that when the sample was annealed at 1100°C, the temperature difference of at least 50°C can cause a significant increase in grain growth whereas the maximum temperature difference was 16°C at 1100°C during annealing of ZnO pellets. As seen in the above section, no dopant contributed to the enhancement of grain growth. This means that such significant increase in grain growth was attributed to the microwave non-thermal enhancement or the microwave effect.

Compared to sintering, grain growth in the a dense ceramic is a simpler process, which just involves the jump of an atom from one side of a grain boundary to the other. In pure conventional heating, it is only driven by the reduction of grain boundary surface energy for the grain growth of an un-doped material system and mass transport is carried out by lattice diffusion and grain boundary diffusion. During microwave hybrid heating the enhanced grain growth suggests that more driving forces contributed to the grain growth. The pondermotive force might be the driving force except the reduction of grain boundary surface energy for grain growth in microwave hybrid heating.

If the driving force for atomic diffusion across the boundary can be taken as the value of the gradient in the chemical potential, $d\mu/dx$, and the pondermotive force, $\langle \rho E \rangle$, see section 2.2.3, and considering equation 2.57, the general driving force can be expressed in the form

$$F_{gb} = \frac{d\mu}{dx} + \langle \rho E \rangle = \left(\frac{1}{\delta_{gb}} \right) \left(\frac{\gamma_{gb} \Omega \alpha}{G} \right) + \langle \rho E \rangle \quad (5.7),$$

where Ω is the atomic volume and $dx = \delta_{gb}$ is the width of the grain boundary. The flux of atoms across the boundary is

$$J = \frac{1}{\Omega kT} \left[\frac{D_{gb} d\mu}{dx} + D_p \langle \rho E \rangle \right] = \frac{1}{\Omega kT} \left[\left(\frac{D_{gb}}{\delta_{gb}} \right) \left(\frac{\gamma_{gb} \Omega \alpha}{G} \right) + D_p \langle \rho E \rangle \right] \quad (5.8),$$

where D_{gb} and D_p are the diffusion coefficients for atomic motion across the grain boundary caused by the gradient in the chemical potential and the pondermotive force, respectively. From equation 5.8, it can be seen that the pondermotive force enhances the flux of atoms across the grain boundary thus accelerating grain growth in microwave heating.

Chapter 6

CONCLUSIONS

6.1. EVALUATION OF TEMPERATURE MEASUREMENT TECHNIQUES IN MICROWAVE HEATING

As Evan [42] said, an effective temperature measurement device should not perturb the microwave field, be affected by the field, or significantly disturb the thermal distribution within the sample. Also, it must be unaffected by sample changes during processing. Additionally, some requirements also needed to be met in the present work, including:

- i) the ability to measure the central temperature of the samples
- ii) reliable temperature measurement in hybrid heating, which means that temperature measurement must be accurate in both conventional heating and microwave heating.

1) Whilst it has been shown that pyrometers can measure the temperature of samples without touching the sample or disturbing the microwave field, a number of factors affect their measurement accuracy, such as the sample's surroundings and their ambient temperature. It is difficult for a pyrometer to be calibrated in the presence of atmospheric gases, windows and suspended material. Additionally, because a pyrometer is sensitive to the emissivity of materials, the accuracy with which they can measure temperature depends directly on the accuracy of the emissivity measurement. In addition, and potentially more seriously, due to reflections from the surroundings

and radiation from elements, a pyrometer can overestimate the sample temperature and it is limited by its inability to measure the internal temperature of the sample.

2) Whilst a thermocouple is a very useful tool for accurate temperature measurement during conventional heating, the presence of the electromagnetic field during microwave processing causes substantial problems. First and foremost, the thermocouple requires shielding from the electromagnetic field, i.e. inserting into a thin walled metal tube. This immediately reduces the accuracy of the device since it makes it larger and more bulky, and in addition it can lead to problems with thermal conduction given that the sample will often be the hottest part of the system. Moreover, and very seriously, the electric field will be concentrated at the tip of the metal probe. This can lead to local heating of the sample, causing significant temperature gradients and thermal runaway, and, if the field is high enough potentially damaging electrical discharges between the thermocouple and sample. All these effects depend on the material's dielectric properties, the microwave power level, thermocouple size and the distance between the thermocouple and the sample. Although these effects are reasonably well understood [42], they appear to be completely ignored by the majority of microwave processing researchers.

3) From the experiment results obtained in the current work, it is clear that the OFT meets most of these criteria provided the calibration of the OFT has been carried out correctly and the probe is shielded from the surrounding radiation by a non-metallic, very low dielectric loss material. Use of the probe to measure the internal temperature of a sample does require a hole to be drilled into the sample, however no technique exists that can avoid this problem. Via the measurement of melting point of vanadium pentoxide, it has been shown that an OFT probe used correctly can obtain accuracy of $\pm 2^{\circ}\text{C}$ in a microwave environment.

6.2. EVIDENCE FOR THE MICROWAVE EFFECT DURING HYBRID MICROWAVE SINTERING

The hybrid heating technique has offered solutions to the challenges in the study of the microwave effect associated with heating ceramic samples with small sizes and low dielectric loss in a microwave field, allowing the effect of different microwave power levels on sintering to be observed and obtaining identical sintering curves under different hybrid heating conditions.

Densification observation of four materials with different loss factors in hybrid heating using different combinations of conventional and microwave power has showed unequivocally that densification was enhanced by the presence of a microwave field and that the enhanced densification increased with increased microwave power level. The validity of the results has been proved via the measurement of temperature gradients, suggesting that the microwave effect is genuine during ceramic sintering.

The results showed that the enhanced level in densification under the same condition was different for different materials and principally was dependent on the dielectric loss, though grain sizes also had an effect. Materials with higher loss factor and smaller grain sizes always showed the greatest enhancement of densification.

In addition, the results also showed that densification enhancement is the most evident in the intermediate stage of sintering, suggesting that diffusional processes are being affected.

6.3. EVIDENCE FOR THE MICROWAVE EFFECT DURING HYBRID MICROWAVE ANNEALING

During annealing of fully dense ZnO ceramic pellets, enhanced grain growth was observed during hybrid heating compared to pure conventional heating. As for the sintering experiments, the greater the microwave power used, the greater the effect in the range 1100°C to 1150°C the grain growth exponent value decreased from 3 during pure conventional heating to 1.4 during hybrid heating using 1000 W of microwave power, suggesting an acceleration of the diffusional processes involved.

6.4. TEMPERATURE GRADIENT MEASUREMENT

No temperature gradient which was greater than 25°C was found in any of the sintered samples that measured 13 mm in diameter and 5 mm in thickness. In addition, the samples heated under conventional conditions always had a higher average temperature than those heated under hybrid conditions and the temperature distribution in the latter was more uniform than in the former. The greatest temperature gradient always appeared at the start of sintering for small samples and became smaller as time progressed. All these results suggest that temperature gradients were not the reason behind the enhanced densification and grain growth observed during microwave hybrid sintering and annealing of ceramics.

An inverse temperature profile was observed in samples with a high loss factor when high microwave power was used. When a hole was drilled in the centre of the sample to allow central temperature to be measured, the large ZnO pellet 25 mm in diameter and 5 mm in thickness, an unusual temperature profile was obtained in which a hot ring was formed between the centre and the edge of the sample during hybrid heating. This suggested that large samples can not be used for observation of the microwave effect when the central temperature is monitored since it is not the highest temperature in the sample.