Sintering of Alumina using Microwaves and Plasma assisted Sintering

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Certificate

This is to certify that work in this thesis has been carried out by **Mr. Umair Saeed, Mr. Atif Javed and Mr. Usama Yaqoob,** and completed under my supervision in Metallography lab, School of Chemical and Materials engineering, National University of Sciences and Technology, H-12, Islamabad, Pakistan.

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Dedication

Our work is dedicated to our family, friends and the faculty of SCME.

Acknowledgement

We thank Allah for the strength and the ability He gave us to complete this project.

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Abstract:

1000 Watt, 2.45 GHz Magnetron, coupled with WR-340 type waveguide is used to sinter pellets of 0.05 micron Alumina powder, made by uniaxial hydraulic press, using Microwaves by focusing them on the pellets. Moreover, three such assemblies are used in combination to generate plasma by utilizing high pressure gas and focusing Iron rod, and using the plasma to attempt to sinter the same powder.

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1. Introduction:

Sintering is a commonly used method in powder metallurgy wherein powder is compacted and densified using thermal means without phase change. The high temperature provided increases the kinetic energy of particles that facilitate in diffusion. The diffusion within the powder particles and across them allow for the powder to grow and fuse into each other, thereby causing the pores to decrease in size. As more time is allowed, the pore size is reduced. Before sintering the compacted powder has a low density due to air entrapment in the pore area, but due to pore size reduction, the density increases of the compacted powder i.e. densification occurs and the density of the compact approaches to that of the theoretical density i.e. the density of solid continuous bulk material, causing an increase in strength and other mechanical properties of the powder.

Electromagnetic waves were first proven to exist by Heinrich Rudolf Hertz, Germany. Initially, it was said that electromagnetic waves were comprised of only wave nature, but later its dual nature was also proven. Hence, Electromagnetic waves are best explained by as particles called Photons, small packets of energy, with a certain frequency associated with them. Moreover, the electromagnetic waves consist of electric as well as magnetic components that are perpendicular to each other as well as to the direction of propagation. These waves can be divided into a spectrum based on the frequency and wavelengths of the waves. These contain Radio waves, Microwaves, Infrared Waves, Visible Spectrum, Ultraviolet waves, X-Rays and Gamma Waves. Each type of wave can interact with matter in different ways.

Microwaves or millimeter waves are types of electromagnetic waves that have wavelength ranging from one meter to one millimeter. Their frequencies, hence range from 300 MHz to 300 GHz. Their energy is lower than X-Rays etc. hence they cannot cause electrical orbital shift. Instead, they can cause mechanical vibrations of the matter they interact with. Microwaves can increase the molecular rotation and torsion, as they are non-ionizing radiation. Due to increase in mechanical vibration, the kinetic energy of the matter increases and hence results in increase in temperature.

Plasma is ionized gas or gaseous ions. Plasma can exist naturally in the atmosphere, 80 km above the Earth's surface. It can also be artificially generated, by different mechanisms such as applying very high voltages across a gas. Examples of plasma are aurora, welding arcs etc. Plasma has high electrical conductivity and due to charge, can be readily influence by electric and magnetic fields. The movement of charged ions also generate their own electric and magnetic fields and in cases can generate electromagnetic radiations. Plasma has very high energy and temperature and generally, unstable if not controlled properly. The main application of plasma is plasma torch that is used for welding or cutting purposes.

2. Literature Review:

2.1. Microwave Sintering:

Sintering is the process wherein a solid mass is formed from a powder using compaction that is application of pressure followed by heating up to a certain temperature. The process of sintering basically involves diffusion. Powder under compaction comes in contact with each other and particles press on each other. Under the application of heat, the diffusion of atoms start, and this diffusion is not just restricted to each particle but atoms may diffuse between particles as well. Individually, powder particles are very small and have a high surface area to volume ratio. In this case, the number of dangling bonds is very high and hence, also the surface energy of the particles which is not preferred. Hence, through diffusion, the particles start to join together, and therefore, the surfaces start to get eliminated. Thus, the driving force for the sintering process is the decrease in Surface energy.

The sintering process involves many different diffusion directions, such as from core of particle to the surface, from the surface towards the point of contact, from surface of one particle to the surface of the other, and from the core of one particle to the core of the other. All these diffusions, specifically those concerned with surface result in necking. The point of contact of particles start to fuse and a single particle is formed and then this point enlarges that is more and more surface starts to fuse, called necking. This occurs over many surfaces and hence, finally many particles fuse into a single one. However, as the orientation of atoms in particles is different, grain boundaries are formed in places of original surfaces.

The density obtained through the sintering process is less than the density of the same material in bulk, because during compaction some pores remain between the particles, which may remain even after sintering. Some pores are closed pores and gas is entrapped in these pores reducing the density of the part. The efficiency and extent of sintering is hence measured by the densification i.e. how close the density of the sintered part can be brought to the density of the bulk material [1].

Therefore densification parameter can be calculated as:

$$D.P = \frac{\text{sintered density} - \text{green density}}{\text{theoretical density} - \text{green density}}$$

Where green density refers to the density of the compacted pallet.

The mode of heating during sintering gives rise to classifications in sintering process, such as Conventional Sintering Methods and Microwave Sintering Methods.

Conventional Sintering methods include heating via Resistance heating, Induction heating or other types, where heat is generated via other methods and then transferred to the sample. This is the indirect transfer of heating and results sintering from outside to inside. Although a simple method, the drawback is that the gas within the pores may get entrapped inside the sample, especially when closed pores are present, and high values of densification cannot be achieved. On the other hand, Microwave Sintering transfers the energy directly to the sample and heating occurs, therefore, sintering occurs from inside out, reducing the chances of closed pores and gas entrapment, resulting in higher densification.

This was demonstrated by Mortaza Oghbaei and Omid Mirzae, during their research, along with effects on sintering time, temperature and grain size distribution in their paper, Microwave vs Conventional Sintering. They found that materials with higher conductivity and permeability show less depth of penetration of Microwaves. Therefore, if particle size is almost equal to the penetration depth, sintering process is more efficient as compared to when the particle size is bigger. Sintering process includes the steps of addition of additives, pressing, heating by some mode. Conventional Sintering uses Induction heating, Resistance Heating or Fossil Fuel heating, however, the heating in this case is indirect. Whereas, in Microwave Sintering, energy is directly transferred into the material which results in volumetric heating, thus a higher potential of high heat-up rates. Microwave Sintering intensifies the diffusion process imperative for sintering. It was concluded that Microwave Sintering required less times due to higher heating rates and resulted in higher densification and better grain distribution and hence, better mechanical and physical properties [2].

In his paper, Microwave Sintering, Brazing and Melting of Metallic Materials, Dinesh Agarwal has discussed his experiments regarding the sintering of different metals which included Aluminum, Iron, Nickel, Cobalt and others. The research also included the use of Microwaves for brazing of metal pieces such as Super Alloy based Turbine blades and melting of certain metals. 2.45 GHz multimode microwave

was used. It was noted that almost all powders can be heated using Microwaves and hence, a lot of powders can be easily sintered as well. The results indicated that by using Microwave Sintering, almost complete densification occurred. This was observed using SEM and optical Microscopy. Moreover, it was observed that the Modulus of Rupture and hardness of the sintered samples increased by a significant value. During the research, the conventional method and the Microwave Sintering method were compared and it was seen that Microwave Sintered samples had a higher ductility because of the spherical or rounded pores that remained whereas in conventional method, the pores were irregular. This was also confirmed by the fractured surfaces of the parts sintered by both methods. The part sintered by Microwaves broke into two flat pieces, and the part conventionally sintered broke into 4 curved pieces [3].
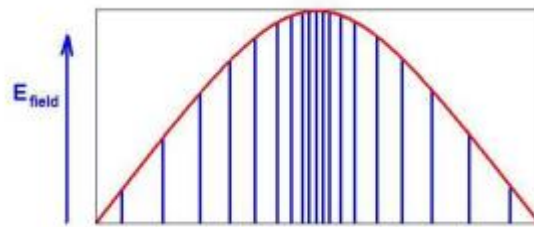
In another of his papers, Microwave Sintering of Aluminum Alloys, D. Agarwal along with C. Padmavathi, worked on two Aluminum alloys, 2712 (Al-Cu-Mg-Si-Sn) and 6711 (Al-Mg-Si-Cu). The research was done to study the effects of Sintering Temperature and atmosphere on the sintering process. Generally, for both alloys, it was noted that as Sintering Temperature was increased, so did the densification. For the alloy 2712, it was observed that if the atmosphere was vacuum during the sintering process, the final density was higher as compared to any other atmospheres, because no gases were allowed to fill the pores or any gas entrapment had not occurred. This was further proven by metallography wherein less porosity was seen and majority of the pores were closed. The alloy also underwent swelling at some points especially when the sintering temperature was higher because of melting of Magnesium, dissolution of Copper and Silicon and formation of intermetallic compounds. For atmospheres of Hydrogen and Argon, densification was lower due to trapped gases. For Alloy 6711, the densification dropped when Nitrogen Atmosphere was used. As compared to sintering of same alloys using conventional method, the energy was saved by 50 percent, and the swelling was also lower [4].

Jipeng Cheng and Yunjin Zhang reported in their paper, Microwave Sintering of Transparent Alumina, their findings on the sintering of Alumina and the effect of MgO additive to the formation of transparent Alumina. They successfully prepared transparent Alumina by Microwave sintering. In contrast to conventional Sintering processes, Microwave Sintering required lesser time and temperature to convert the

polycrystalline Alumina to single Crystal Sapphire. Without MgO, at high heating rate and 5 minutes' time by Microwave Sintering, lots of small pores remained and the grain size was high. It also showed Fine cracks, and partial translucency, concluding that MgO is imperative for fabrication of transparent Alumina. The research also exhibited that Sintered Alumina shows secondary phases. However, by Microwave sintering, densification and grain growth can be enhanced and full densification was achieved by sintering at 1750^0C for 15 minutes [5].

2.2. Plasma assisted Sintering:

The electric field of the microwave can predicted in a waveguide. The waveguides guide electromagnetic waves passing through them. If the microwaves are of 2.45 GHz, rectangular waveguides are used

Figure 1: The electric field component across the cross-section of waveguide

and the wave mode is TE10 mode (Transverse Electric Field mode). The mode determines the electric field and magnetic field components within the waveguide, as shown.

The electric field becomes maximum become maximum at the half length of the width.

TE10 mode means transverse electric mode, which means that the electric component of the electromagnetic wave moves across the waveguide perpendicular to the direction of propagation of wave and the waveguide length. The (10) in TE10 means that the width of cross section of the waveguide is equal to one half wavelength of the wave, whereas the height is shorter
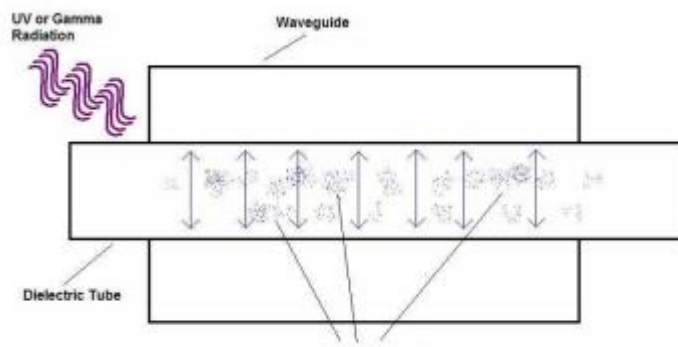

Figure 2: Initiation of Plasma in presence of UV or Gamma Rays and movement of electrons.

than one half wavelength, typically used height equals one fourth of the wavelength of the wave, which for 2.45 GHz translates to 3.4 inches into 1.7 inches cross-section.

Plasma can be generated by focused microwaves. When microwaves through an Aluminum waveguide over a conducting wire, the electric component is highest over the point where the wire lies [7]. Conducting wire acts as a dipole antenna. The background Ultraviolet and Gamma Radiation causes free electrons in the gas to oscillate. The random motion of electrons in the gas in contributed by the collisions of electrons with the gaseous atoms. The electrons are further accelerated and undergo forced motion by the electric field of the microwaves. The electrons, when collide with the atoms elastically, they change their direction, and if at this time, electric field changes direction, the electron has high enough energy to knock out the electrons from the neutral atoms [8]. The plasma is hence ignited, and maintained by continued provision of microwaves i.e. energy.

Another plausible mechanism is when a focused beam of microwaves strikes with the tip of the metallic wire, it excites its energy state resulting in the ejection out of an electron from the wire. This electron keeps colliding with the molecules of introduced neutral gas and ionizes the gas molecules by ejecting their electrons. These electrons further aid the generation of plasma by ionizing further gas molecules. Thus, it can be said that plasma generation is a chain process.

The quartz tube within which the conducting wire is placed along with the high pressure gas flowing downwards directs the plasma which escapes from the bottom of the tube, creating a plasma torch. This torch has a very high temperature and can be used for different purposes.

Quartz tube and Boron Nitride cylinder can also be used. The condition is that the material must be transparent to the microwaves. But another condition is that the cylinder must also be transparent to visible and Ultra-violet radiations. These conditions are fulfilled by the Quartz, hence, Quartz is used.

In his article, Microwave discharges: generation and diagnostics, Yu. A. Lebedev states that it is common practice to use microwaves for generation of quasi-

equilibrium and non-equilibrium plasma that can then be used in different applications. If the incident power ranges between several Watts to hundreds of kW and pressures range from 10^{-5} torr to atmospheric pressures, plasma can be generated in pulse and continuum wave regimes, with utilization of up to 90 % of the incident power for generation of plasma. The quasi-equilibrium and non-equilibrium plasma can be generated in wide range of pressures in Microwave plasma generators, using a wide range of gases that can be Argon, Nitrogen, and Oxygen etc. [9].

In his paper, Sintering, consolidation, reaction and crystal growth by the spark plasma system (SPS), Mamoru Omori says that Spark Plasma System (SPS) works on the principle of using an electric discharge to generate plasma that can then be used for sintering of metals and even ceramics. Sintering by plasma could facilitate in research of advanced materials. The equipment was later patented in America, but after the expiration of the patent, many SPS equipment were fabricated. SPS contains five merits to be considered. First is the generation of spark plasma which can be thought of as a way of manufacturing new materials. Second is the effect of electric fields, and the third is correlated and considers the effect of electric current or skin current in conductors or semiconductors and insulators respectively. Fourth is the impact of spark plasma that give rise to mechanical forces but is not significant and can be ignored. Last is the rapid heating and cooling that defines the efficiency of heat treatment [10].

Fast Densification of Ultra-High-Temperature Ceramics by Spark Plasma Sintering by Alida Bellosi, Frederic Monteverde and Diletta Sciti discusses that SPS was investigated to check its suitability and efficiency to produce HF and Zr borides that were ultra-high-temperature-based. The microstructures and properties were studied to evaluate the effects of processing techniques. As compared to hot-pressing techniques, SPS showed the advantage that poor sinterable powder compositions could easily be sintered and parts fabricated in short time, all this in the absence of a sintering activator, unlike in hot pressing. Ultra-high temperature ceramics in the systems HfB_2-SiC, ZrB_2-$MoSi_2$ as well as ZrB_2-ZrC-SiC could be densified using both hot pressing as well as SPS. However, SPS took shorter sintering times to obtain the same densification, i.e. 20 minutes vs 2 hrs. for hot pressing, and without any activators for sintering. This presented opportunities to use SPS in sintering of high-dense ultra-refractory ceramics by SPS, as well as made possible the

optimization of SPS system to control the conditions necessary for sintering of different compositions [11].

In their paper, Spark Plasma Sintering of Alumina, Zhijian Shen, Mats Johnsson, Zhe Zhao and Mats Nygren investigated the effect of various parameters of SPS which included temperature, holding time. Pressure, heating rate and pulse sequence. The effect of these parameters is directly on densification, hardness, fracture toughness and grain growth. Hence, the effect was studied on sub-micrometer-sized Al_2O_3 powder. SPS process was found to increase both the densification and grain growth kinetics. Hence, this method could densify Alumina up to 99.8% at much lower temperatures of 1150^0C within a matter of minutes. It was found that densification was enhanced in the initial stages by local spark-discharge processes around the particles' contacts. The electric fields generated die to pulsed DC also enhance the grain boundary diffusion and migration, which are largely dependent on temperature. Hence, using SPS, if sintering temperatures can be lowered, the original fine-grained structure can be maintained even in the fully densified body [12].

3. Characterization techniques:

3.1. Scanning Electron Microscope:

Scanning electron microscopy (SEM) is used to study the morphology and phases present in the material. SEM scans a focused electron beam over a surface to make an image. When electron beam is focused on a sample surface electrons interact with the sample therefore various signals are produced that can be used to retain information about the surface topography and the phase composition.

Some analysis that can be done using SEM:

- Identification of materials
- Compositional analysis
- Topographical features, Morphology
- Phase distribution and crystal orientation
- Presence and location of defects. Failure analysis

- Elemental composition of micro-volumes with energy dispersive spectroscopy (EDS)

Working of scanning electron microscope involves first sample preparation. The samples are first attached over a holder using double sided carbon tape thereafter the samples are gold sputtered to increase the conductivity of electron beam through the sample.
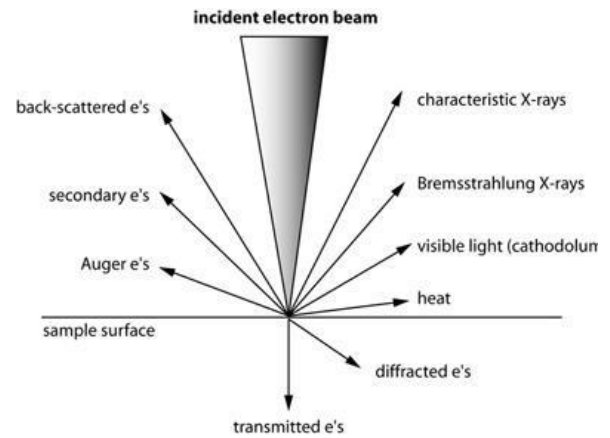

Figure 3: Interaction of electrons with matter.

Scanning electron microscopy is conducted by bringing a sample in contact to an electron beam [13]. A powered electron gun generates a beam of electron with specific energy. Magnetic condensers are used to focus the beam and a specified rectangular area of specimen surface is focused. Interaction of the electron beam with material generated different signals which depends on the sample, i.e. backscattered electrons, auger electrons, photons, secondary electrons, etc. Specific special detectors are used to detect different types of signals being produced. [14]
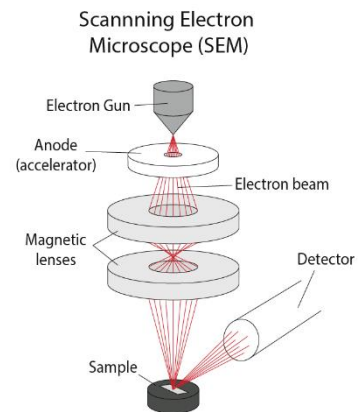
Figure 4: Schematic of SEM.

Signals are amplified to produce a magnified grey-scale image of the sample with extremely high resolutions in nanometer range. Magnification of scanning electron microscope is independent of the lens and is defined as the ratio of length of scan line on monitor and length of scan line on specimen. Thus the magnification is adjusted by changing the size of area of the specimen being scanned, i.e the smaller the size higher would be the magnification.

Amount of signals detected from the surface vary due to difference in electronic densities of elements being used. The higher the atomic number of the element being scanned the more electrons are present and thus the interaction is larger therefore the elements with higher atomic number appear brighter than the lower atomic number elements.

SEM is performed on JEOL scanning electron microscope (JSM 6490LA) available in SCME. 5-20 kV operating voltage is used with spot size in the range of 30 to 55 and around 10mm of working distance is maintained.

3.2. X-Ray Diffraction:

X-Ray Diffraction is a non-destructive analytical technique used to identify the crystal structure of materials or phases present.

As the properties of materials are linked back to the atomic arrangement in crystals therefore the study of crystallographic structures and lattice parameter is of primary importance. For this XRD is used. Crystalline structure comprise of planes of atoms which reflect the incident X-Rays on it at a particular angle, this phenomena is used to detect the d –spacing, planes and structure of a material.

When X-rays generated by Copper in cathode ray tube are filtered and incident on the sample, their interaction produces constructive interference which when satisfies Braggs Law are detected, processed and analyzed.
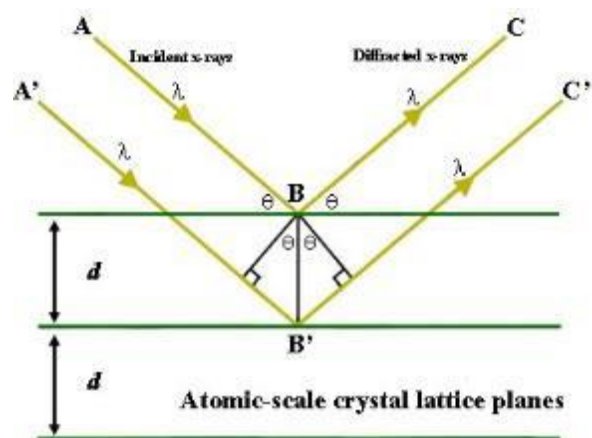
Figure 5: Bragg's Law.

Bragg's Law: *nλ=2d sin θ*

Where, n is order, λ is wavelength, d is the inter planner spacing and θ is the angle of incident beam.

This law relates wavelength of electromagnetic radiations to the lattice spacing in crystals and diffraction angle.

The sample is scanned in the range of 2θ so that all possible orientations and diffraction directions are attained. The machine measures angle 2θ by default as shown in the figure.
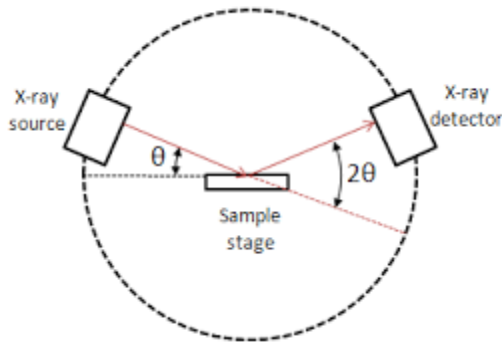
Figure 6: Schematic of XRD setup.

Diffraction peaks can be converted to d- spacing this allows identification of the crystal structure and thus the materials because each crystal has its own unique d-spacing. This d-spacing is then compared with standard reference patterns available as cards in the reference library. [15] [16]

Limitations of XRD:

- If a materials to be identified is completely unknown it should be pure homogenous and single phase material.
- If less than 2% of a phase is present it is not identified by XRD
- Sample preparation induce stresses in the materials thus change in d-spacing resulting in shifted peaks [17].

3.3. Micro Vickers Hardness test:

Hardness is defined as a resistance of materials to indentation. That is, if we apply load to a material how hard it is to indent the materials determines the hardness of the materials. Usually hardness measurement through indentation is done by measuring the size or depth of indentation. Vickers test also known as micro-hardness test due the specifications it uses to measure hardness of specimen small in size and depth. Therefore sample preparation is also an important requirement for the Vickers test as the surface of the sample needs to be smooth and sample small enough in size to fit the apparatus, therefore sometimes mounting is also required to hold and deal with the sample easily.

Optical measurement is used to determine hardness by Vickers test. The procedure is as follows; square based diamond shaped indenter is loaded to the sample with small load of up to 30kg. This produces an indentation or mark on the specimen which then using optical microscopy is measured in size as shown in the diagram. The dimensions are then substituted in the formula given to calculate the hardness value.
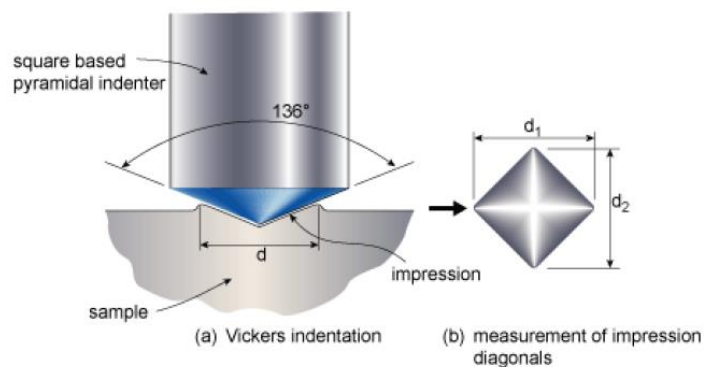

Figure 7 Schematic of Vickers Hardness Test

The formula used for calculating hardness is:

$$\text{DPH} = \frac{2P\sin(\theta/2)}{L^2} = \frac{1.854P}{L^2}$$

Where, P is applied load in kg L is average length of the two diagonal in millimeter Θ is the angle between opposite faces of the diamond indenter that is 136o

4. Experimental Procedure:

4.1. Design and fabrication of Machine:

The parts used in Construction of furnace are

- Three Magnetrons (1000 Watts-1200 Watts)
- Three sets of transformer, capacitor and rectifier
- Three waveguides
- Quartz tube
- Metallic box
- Wires and Power Supply

Figure 8: Microwave Sintering Oven

Waveguide resembles a hollow metal piper. It usually has a rectangular cross section, but the choice can also be extended to a circular or oval cross section. They work similarly to focus microwaves as a water pipe would for water. The microwaves travel through the waveguide, from one component to the other. The advantages of waveguide include high power handling capabilities and low attenuation but are limited due to their size and limited bandwidth.

If the walls of the waveguides are fabricated using perfect conductors, microwaves cannot penetrate into the walls. But the walls are not perfectly conducting and hence the waves can penetrate into the walls. The depth to which the waves can penetrate is termed as Skin depth. This depth is related to frequency.

$$Skin\ Depth = \delta_s = \sqrt{\frac{2\rho}{2\pi f \mu_0 \mu_R}}$$

where :

$\rho = bulk\ resitivity\ (ohm - meters)$

$f = frequency\ (Hertz)$

$\mu_0 = permeability\ constant\ (Henries\ /\ meter) = 4\pi \times 10^{-7}$

$\mu_r = relative\ permeability\ (usually \sim 1)$

Waveguide used is WR-340 type waveguide that is used as standard for 2.45 GHz microwaves. The inner dimensions of the waveguide are 3.4 inches by 1.7 inches in

cross section. The waveguide used is made up of Aluminum sheets of thickness one millimeter. The waveguide used is also tapered to concentrate to concentrate the microwave power in a smaller cross section. Furthermore, the waveguide is single tapered, i.e. the taper length is equal to the guide wavelength, to minimize the reflection.

By calculations, the skin depth of 2.45 GHz microwaves for Aluminum is 0.2 mm.

Waveguide is terminated using short circuit plates. The antenna side short circuit plate is placed at one quarter of the guide wavelength from the antenna on the opposite side of the magnetron to establish TE10 mode. At the load side, the plate is again placed at one quarter of the guide wavelength to produce standing waves, for maximum amplitude at the tip.

Figure 9: WR 340 Waveguide

4.2. Sintering of Alumina:

Sintering of Alumina pallets is done in Microwave furnace. The furnace comprises of 800 W, 2.45 GHz magnetron coupled with a WR-340 type waveguide (85mm x 45mm cross section) with tapered and shorted sides. The Microwaves are focused into a quartz tube into which the pallets are inserted and placed via the aid of a rod. All equipment is shielded by Aluminum foil including the rod used for insertion, to prevent Microwave leakage and heating of equipment.

To make pallets of Alumina powder, different particle size is used. Pallets of 30 micron, 1 micron and 0.05 micron Alumina powder are formed via unidirectional hydraulic pallet press. The die for the process is of 10 mm diameter and consists of a

die and pushing rods, one of which is longer referred to as plunger and the other one smaller in length. Die is made of D2 die steel which has the following composition:

Carbon	Manganese	Silicon	Chromium	Molybdenum	Vanadium
1.50	0.30	0.30	12.0	0.75	0.9

Table 1: Composition of D2 Die steel

The Alumina powder is first grinded in Agate Pester and Mortar set, to reduce the agglomeration of Alumina powder that may have occurred over time. This is done for an extended period of time i.e. one hour. No additives are added into the powder.

Before making pallets, the die is properly washed and cleaned, first by using running water and then by applying acetone onto a tissue paper and rubbing it on the die. This is to remove any contaminants on the die which may affect the powder properties, Pallet making capabilities or increase friction within the die during application of pressure. Next is the application of Oleic Acid on all components and their faces of the die. This ensures minimum friction between the parts of the die and prevent powder from sticking inside the die cavity or on the pushing rods. This also ensures that maximum and uniform pressure is distributed over the powder.

Figure 10: Alumina pellets

The die is then placed in the unidirectional Hydraulic press and the shorter pushing rod placed inside the die cavity as a base. After that, the powder is poured in the cavity and finally the plunger over it. The lever in the hydraulic press is then used to apply the pressure.

The powder used for each pallet was 0.85 grams which was measured using electronic mass balance. The pressure applied was 1.5 tons for 10 seconds. After the desired time period, the pressure is released from the control knob and the die is removed. It is inverted and placed along with the evacuation ring over the die into the press, and pressure is again applied. In this case, pressure required is very low; and the shorter pushing rod and the pallet is evacuated from the die.

The density of each pallet is then measured using Archimedes Principle before sintering to be compared with the density after sintering. The mass of the pallet is first measured in air and noted using a mass balance. The mass of the
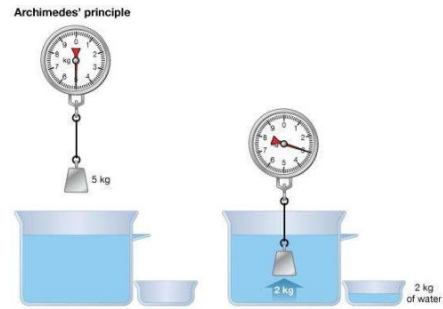

Figure 11: Archimedes Principle

pallet is then measured in water by using mass balance over which a water bath is placed. A tray is immersed in water and supported by a rod. The mass balance is then set to zero and the pallet placed on the immersed tray. The mass of the pallet is recorded to be less than that when measured in air. This value is actually the value of (mass * density) hence volume. Mass measured in air is divided by this volume to get the densification.

$$Densification = \frac{density\ of\ unsintered\ pellet}{theoretical\ density}$$

After the density measurements, each pallet is sintered in the microwave furnace. Three pallets are placed on top of each other over the supporting rod and inserted into the quartz tube. Between each pallet, a little powder is sprinkled in order to avoid the sticking of the pallets. In principle, the pallet in the middle will be better and properly sintered, whereas the other two pallets will not be considered as effective samples. The magnetron is turned on and the time is varied between 1 hour and 5 hours.

Multiple pallets are sintered, with the variation of sintering time between each pallet to observe the relationship between sintering time and the densification. Only the middle pallets will be changed, the other two can be used repeatedly.

After sintering, the density of the pallets are again measured using the same method and the initial density, final density and the density of bulk Alumina are compared in order to know the extent of densification and the efficiency of sintering procedure. Moreover, their porosity is calculated using the formula:

$$Porosity = 1 - \frac{density\ of\ unsintered\ pellet}{theoretical\ density}$$

Each of the sintered pellets are then characterized using Scanning Electron Microscope to observe the pore size at the surface and time based microstructural evolution during microwave sintering. Moreover, X-Ray diffraction is used to observe the shifting of peaks and hence, the recrystallization and regrowth of grains.

Vickers hardness test is used to check the hardness of the pellets. However, as the pellet is of ceramic and brittle, micro Vickers hardness test is used. Due to no visibility of the indent in the microscope, the indent has to be observed under SEM and its diagonals measured, and hence the hardness in Vickers hardness number. A line is drawn on the pellets using a pencil and multiple indents are taken on the pellet along the line. This is to easily locate the indents during SEM and to take the average for reduced error.

4.3. Plasma assisted Sintering of Alumina:

Microwaves are used to generate plasma inside the quartz tube using the three assemblies of 1000 Watt magnetrons coupled with waveguides, and a focusing Iron wire, with the aid of Argon gas at high pressure.

Pellets are made in the same way and their green density measured using Archimedes Principle. The stage for the pellet is placed below the microwave oven which is composed of ceramics. The pellet is placed and set below the oven before the plasma is produced.

To turn on the plasma torch, first the valve of the Argon gas cylinder is opened, such that the axial gas flow is set to 5 liters per minute, ensured by the needle valve. The power supplies of all magnetrons are turned on. The Iron wire is then inserted into the quartz tube from the top till the opening of the bottom most waveguide, and the plasma is formed.

The plasma formed is in the form of a torch, directed downwards from the bottom opening of the quartz tube. Pellets are in contact with the plasma and heat up due to it. Different pellets are then allowed to stay there for different periods of time. After the decided time, the plasma torch is turned off and the pellet allowed to cool.

The pellets' density and densification are then measured and calculated, and each pellet characterized using the same techniques.

5. Results and Discussions:

5.1.   Microwave Sintering:

5.1.1.   Densification measurements:

Mass of pellets: 0.85 g

Theoretical density: 3.9 g/cm^3

Figure 12: Sintered pellets.

Time/hours	Mass/g	Volume/cm^3	Density/ g cm^{-3}	Densification (%)	Porosity (%)
0	0.85	0.6439	1.32	33.8	66.2
0.5	0.85	0.5667	1.50	38.5	61.5
1	0.85	0.3972	2.14	54.9	45.1
1.5	0.85	0.3346	2.54	65.1	34.9
3	0.85	0.2901	2.93	75.1	24.9
5	0.85	0.2665	3.19	81.2	18.8

Table 2: Change in measured volume and calculations of porosity for different sintering times
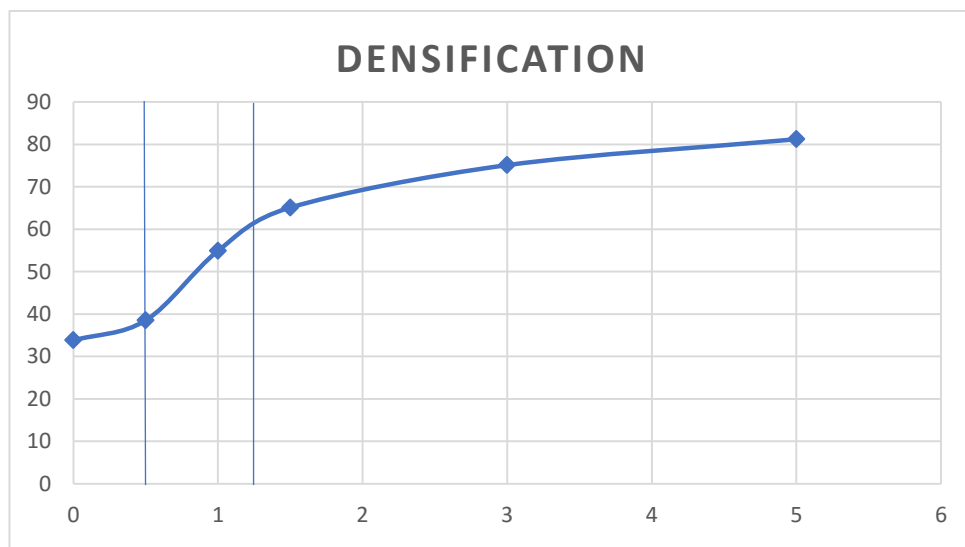

Figure 13: Change in Density with sintering time.

The density of the pellets increases as the time proceeds. The unsintered pellet has the density of 1.32 g/cm^3, which means that the pellet had high porosity i.e. 63.2 %. As time of sintering increases, the density of the pellet approaches that of bulk density, and densification increases. However, the densification increase is not linear, instead from time 0 hours to 0.5 hours, the increase is slow. At 0.5 hours, the densification rate increases dramatically upto 1 hour and 20 minutes and the density reaches upto 2.5 g/cm^3. The densification rate again decreases and keep on decreasing till the end of 5 hours, giving the final density of 3.9 g/cm^3.

The graph can be divided into three parts thereby. These parts correspond to three stages of sintering that can be affiliated with different processes, and are commonly observed in sintering process in general.

- **Stage 1: Initial Neck Growth**

  The particles start to join together at the points of contacts, and grain boundaries start to form at these points through diffusion. Hence at these points of contacts, necks begin to form. No decrease in dimensions can be observed and density changes very little as nor densification occurs significantly.

- **Stage 2: Intermediate Sintering Stage**

  The adjacent necks start to impinge upon each other. Densification and grain growth occurs during this stage. This stage also includes pore channel closure, that is interconnected pores are isolated due to neck growth and creation of new contact points, due to pore shrinkage.

  Grain Boundary Diffusion, volume diffusion and other bulk transport mechanisms dominate in this stage, i.e. material gets transported from the bulk towards the boundaries.

- **Stage 3: Final Stage**

  The pore size is reduced very much and the network of pores is broken down into smaller, isolated pores. The densification in this stage is much slower as now the material has to be transported into the pores. This is a very time consuming process, given that the gas entrapped in the pores have means to escape.

5.1.2. Scanning Electron Microscope

1 hour

3 hours

5 hours

Table 3: SEM images of sintered pellets.

The SEM images show the microstructure for different times of sintering. Three different times of sintering are chosen to see the time based microstructural evolution by microwave sintering. The pore size is measured using SEM.

As the time for sintering increases, the pore size decreases which corresponds with the decrease in porosity. The pore size decreases from 88 nm for 1 hour of microwave sintering to final 59.71 nm for 5 hours of microwave sintering. This further helps conclude that sintering is effective. Moreover, the size of the pores

decrease but they increase in number because due to necking, one pore may convert into multiple particles.

Another observation was made, that the particle size seems to decrease. This observation is due to the fact that sintering causes mass flow between the particles via diffusion. As both bulk and surface diffusion processes are occurring, mass flows from the particles towards the necking regions. This causes the particles to join together and form ligaments. This can be observed in SEM images and the ligaments grow in length as the sintering time increases. However, as the mass decreases from the core of the particle and increases in the necks, the overall particle size decreases.

Another observation is that the surface is getting homogenous with respect to its morphology that is the amount of contrast is decreasing that is indicative of grooves. Moreover, the particle size is getting more uniform or similarly sized particles are observed at higher sintering times. This shows that Oswald ripening is occurring which is a characteristic process during sintering.
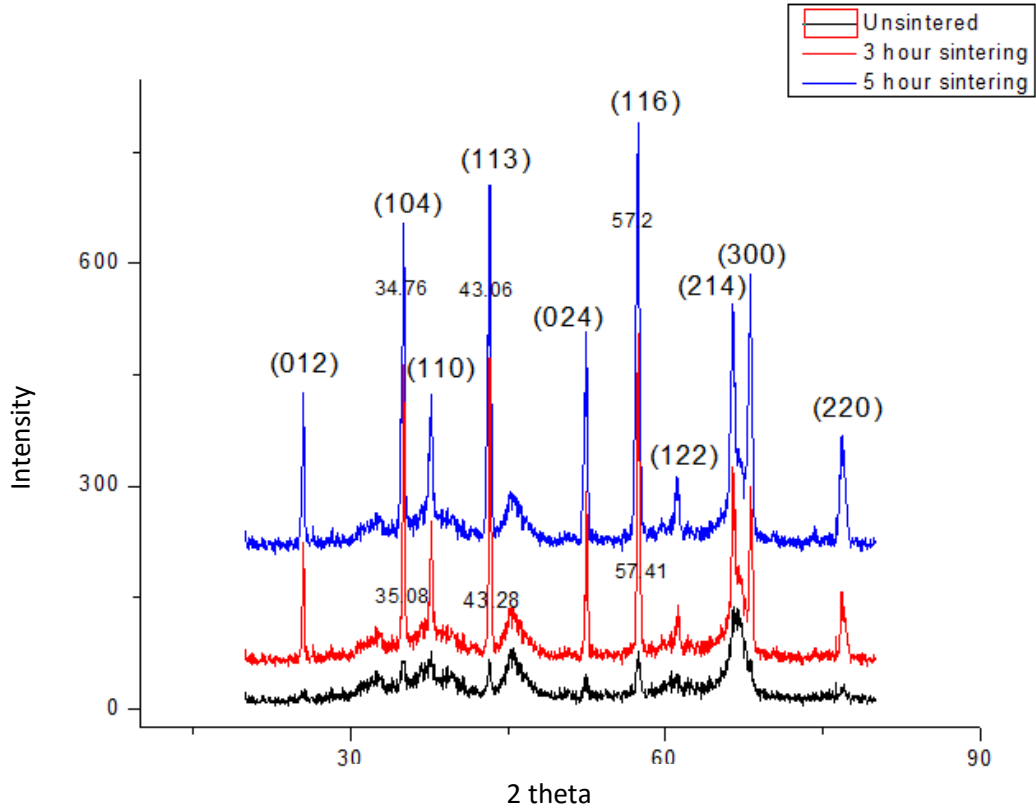
5.1.3. X-Ray Diffraction:

Figure 14: XRD patterns of unsintered, 1 hr. and 5 hr. sintered pellet.

XRD results show the patterns for unsintered pellet, 3 hour sintered pellet and 5 hour sintered pellet.

The pattern for unsintered pellet is typical of a polycrystalline nano-powder. It shows peaks which are broad and is generally not showing and characteristic peak.

The XRD patterns of 3 hour sintered pellet and 5 hour sintered pellet show characteristic peaks of planes and show exactly the same peaks. However, there is a slight shift of all peaks to lower 2 theta values as the sintering has proceeded from 3 to 5 hours.

The shift in peaks is due to the change in lattice parameter. The decrease in 2 theta values show that the lattice parameter has increased. This corresponds to the removal of vacancy defects in the crystals. Vacancies in the crystal cause a localized compressive strain that results in the reduction of lattice parameter for the plane in which the vacancy is contributing to.
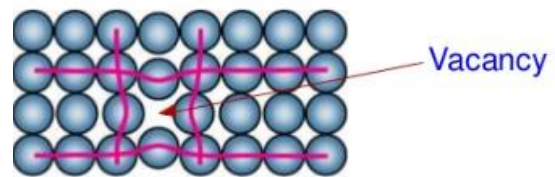

Figure 15: Compression Strains due to vacancy

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As the sintering proceeds, diffusion of atoms causes these vacancies to be filled because they are thermodynamically less stable than a perfect crystal. Hence, when these vacancies are removed, the strains are removed as well and the lattice parameter increases, as indicated by the shift in peaks within the XRD pattern.

Another important aspect of XRD is the calculation of inter-planar spacing of the planes. This was done for two planes: (104) and (116). The d-spacing can be calculated for Alumina using the Bragg's law and knowing that Copper k-alpha wavelength was used. The following results are obtained:

Plane	3-hour sintered pellet		5 hour sintered pellet		Perfect lattice
	2 theta	d-spacing	2 theta	d-spacing	d-spacing
(104)	35.08	25.6 nm	34.76	25.76 nm	26.83 nm
(116)	57.32	16.06 nm	57.2	16.12 nm	17.89 nm

Table 4: Calculation of d-spacing of two example planes

These results indicate that as sintering is proceeding, the lattice parameter is approaching that of perfect lattice. Therefore, it can be concluded that defects are being removed, and the crystallinity of the pellets is improving. Moreover, as the relative intensities of the peaks do not change, it can also be concluded that no preferential plane growth is occurring.

5.1.4. Micro-Vickers Hardness Test:

Two indents were taken on each of the three pellets that is 1 hour sintered pellet, 3 hour sintered pellet and 5 hour sintered pellet. The diagonal lengths of the pellets are shown in the table. The force used was 1 kgf.
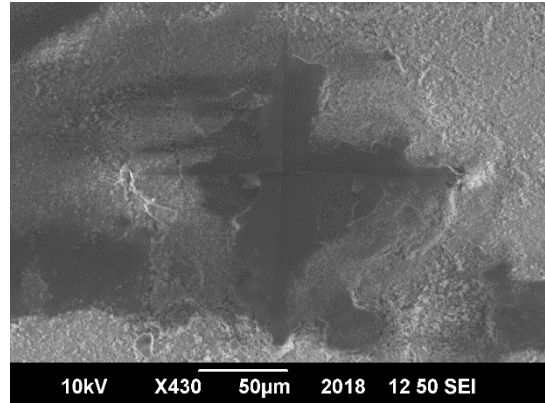

Figure 16: Micro-Vickers indent on 5 hr sintered pellet as seen through SEM.

Pellet	Indent 1 (mm)		Indent 2 (mm)		Average	Hardness
	Diag. 1	Diag. 2	Diag. 1	Diag. 2		
1 hr.	0.1963	0.1968	0.1961	0.1972	0.1966 mm	479.8 kg/mm^2
3 hr.	0.1755	0.1753	0.1751	0.1749	0.1752 mm	604.1 kg/mm^2
5 hr.	0.1433	0.1430	0.1431	0.1430	0.1431 mm	905.6 kg/mm^2

Table 5: Lengths of Diagonals of indents by Micro-Vickers

The hardness of the pellets increases with sintering time. This is because of the sintering process, as the powder get compact and the ligaments grow, the porosity decreases, the pellets harden and the hardness approaches that of bulk Alumina. The hardness of the unsintered pellet was not measured because, the unsintered pellets broke under micro-Vickers indenter.

The hardness of bulk Alumina with grain size of 0.05 microns, similar to our powder size is 1187 kg.mm^2. The hardness due to sintering approaches this hardness, but requires more time to reach this. However, the final hardness may not exactly be the same, because hardness depends on grain size as well and sintering of 0.05 microns powder may not result in the grain size of 0.05 microns. The sintering may produce a grain size larger than 0.05 microns and hence the hardness will be lower.

5.2.   Plasma assisted Sintering:

Plasma assisted sintering could not be done on the pellets. The setup used comprised of three magnetrons coupled with waveguides, to focus microwaves within a quartz tube, and an iron rod to focus the microwaves to generate a spark to produce plasma. The gas used was Argon gas that was input into the quartz tube at a very high pressure of 5 liters/minute.

The gas input was first turned on. When the magnetrons were turned on with the iron rod inside, spark was generated. The plasma was generated as well but for a short period of time that amounted to only 6 seconds. During this time, temperature increased which melted the tip of the iron rod. This caused the sharp end of the rod to be lost and microwaves could no longer be focused and spark was lost.

Generally, once when plasma is generated and sustained, plasma can sustain itself even without the rod because of high energy collisions within the plasma. However, in this experiment, within this period, the plasma generated had not become self-sustaining and hence, plasma generation was lost.

The iron rod tip was sharped again using grinding, and the test re-run, but the results were same, and plasma torch could not be sustained. Therefore, the plasma assisted sintering was not achieved.

6. Conclusion and Future Recommendations:

The sintering process was a success and 81.2% densification was achieved using a lab fabricated equipment of microwave sintering. This was achieved in sintering times of 5 hours which can be considered very efficient as well when compared to sintering in muffle furnace that takes approximately 14 hours. However, there are many drawbacks such as thermal cracks and uncontrolled heating.

The plasma assisted sintering was not achieved due to the melting of the Iron rod and hence losing the focusing of microwaves to create a spark to generate plasma.

There are many improvements that can be done on the equipment for better results.

First, the problem is thermal cracks. They appear due to uncontrolled cooling. When the magnetron is turned off or the plasma torch is turned off, the pellet cools in open layer which is fast. Due to the uncontrolled cooling, differential cooling and hence, contraction occurs and thermal cracks may appear. In the future, a system of controlled cooling may be introduced such as proper insulation for the pellet holder to the equipment.

Another problem is the limit to which sintering can be done in terms of densification. It was observed that as time of sintering increases the densification rate decreases, i.e. for the first hour of sintering, the densification was higher than the last hour. This is due to the limit in power of magnetrons. Hence, larger power rated magnetrons may be incorporated into the equipment to reach higher densification values.

To sustain plasma, tungsten rod may be used that has a much higher melting point, hence, avoiding the melting of the rod before sustaining the plasma, or melting altogether.

In the present equipment, there is no way to measure the temperature that is reached within the machine. Hence, a mechanism may be introduced that can measure real time temperature changes and its change with respect to time. This can be done using a pyrometer that is focused over the pellet.

The limitation to the Quartz tube is that it cannot incorporate certain shapes and sizes into itself for microwave sintering, hence, this may be changed or replaced by a bigger quartz tube, but also accompanied by a different magnetron and waveguide.

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