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Single-Mode Microwave Sintering of Traditionally Resistant Materials

by Victoria L Blair, Selva Vennila Raju, Mike Kornecki, and Raymond E Brennan

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by Victoria L Blair and Raymond E Brennan
Weapons and Materials Research Directorate, ARL

Selva Vennila Raju
Oak Ridge Associated Universities, Aberdeen Proving Ground, MD

Michael Kornecki
SURVICE Engineering, Aberdeen Proving Ground, MD

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14. ABSTRACT Microwaves can be effectively exploited and controlled by designing a sample chamber with a resonant cavity that produces a standing wave in which the electric and magnetic field components are spatially separated. This can lead to distinct regions in which the sample can be positioned for exposure to a specific set of microwave conditions (100% electric, 100% magnetic, mixed ratio of electric-to-magnetic). Processing of ceramics under microwave frequencies has been pursued for several decades, but success has been dictated by the limited number of ceramics that readily couple with microwave fields. Compatible ceramics generally have high dielectric losses, which cause heat to build up in the material, promoting uniform densification and fine grain structures. However, most materials are not microwave-susceptible and require an external susceptor to harness the microwave energy and transfer the heat to the sample. Alternatively, internal susceptors can provide localized heating of microwave-transparent ceramics, thereby reducing sintering times and helping to maintain a finer grain size. In this work, efforts to blend hybrid ceramic materials composed of microwave-transparent materials and ferromagnetic materials (which act as internal susceptors) are pursued to obtain dense materials with fine microstructures. Microwave sintering of alumina using microwave-susceptible nickel ferrite plate yielded a density only 8% greater than the original green density, whereas use of nickel ferrite as an internal susceptor forming a ceramic composite increased density by 22% at a lower temperature than the external susceptor sintering method.					
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1. Introduction

1.1 Microwave Sintering

Microwave sintering of materials has been employed since the late 1970s, when its most notable use was for the production of cobalt-cemented tungsten carbide (WC-Co) cermets for the oil and gas industry.^{1,2} It was observed that the cobalt binder phase coupled well with microwave energy, and heating to its melting point would result in liquid phase sintering of the part. The microwave-sintered parts were found to have a finer final grain size as a result of faster heating rates in comparison to radiant heating methods.³ The methods used in this process were multimode microwave sintering techniques, in which tens to hundreds of microwave modes were excited and reflected in a cavity. This is the same technology used in microwave kitchen appliances—systems that typically suffer from hot spots and require turn tables to achieve uniform heating. For this reason, many microwave systems employ multiple magnetron heads, or external susceptors, to uniformly heat parts. Recently, commercial industries have been developing hybrid heating systems in which magnetron heads are added to thermal radiation heating furnaces to obtain faster heating rates typical of microwave sintering.⁴

Radiant sintering methods rely on resistive heating elements in which the temperature increases as the electricity flows through the elements. The heat must then transfer to the material being sintered through the surrounding atmosphere. This naturally leads to an outside-in heat gradient through the part, with the sample's heating rate dictated by the thermal conductivity of the part. Microwave sintering has a different mechanism, as microwave-susceptible materials heat internally (inside-out) due to a moderate to high dielectric loss ($\tan \delta_e$).^{3,5-9} The magnitude of the dielectric loss of the material is directly related to the heating rate of the material. The exact mechanism of the internal heating due to microwaves is unknown. However, the prevailing hypothesis is that dipole reorientation leads to the heating, which occurs in materials with sufficiently high dielectric loss.⁴

Single-mode microwave sintering is a process in which the electric and magnetic field components of the microwave are spatially separated within a specially designed cavity. The system is set up such that the magnetron head is oriented in the direction of a waveguide, which confines and propagates microwaves toward a resonant cavity. This resonant cavity has dimensions that match the microwave and produce a standing wave.¹⁰⁻¹² This results in the orthogonal separation of electric and magnetic components of the wave, as shown in Fig. 1.

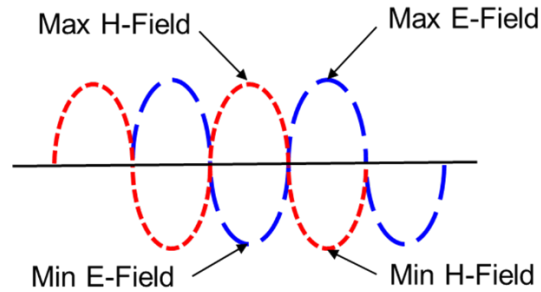


Fig. 1 Two-dimensional representation of the electric and magnetic field distributions within a microwave cavity; the minima and maxima of each field are noted

Single-mode systems have the benefit of process control through tailoring of exposure to electric or magnetic energy.¹² If the material is not susceptible to magnetic energy, it can be subjected to a mixed field mode (combination of electric and magnetic energy) and heated with electric field energy while still being exposed to some magnetic energy. A comparison of multimode, single-mode, and mixed-mode microwave sintering methods is shown in Fig. 2.

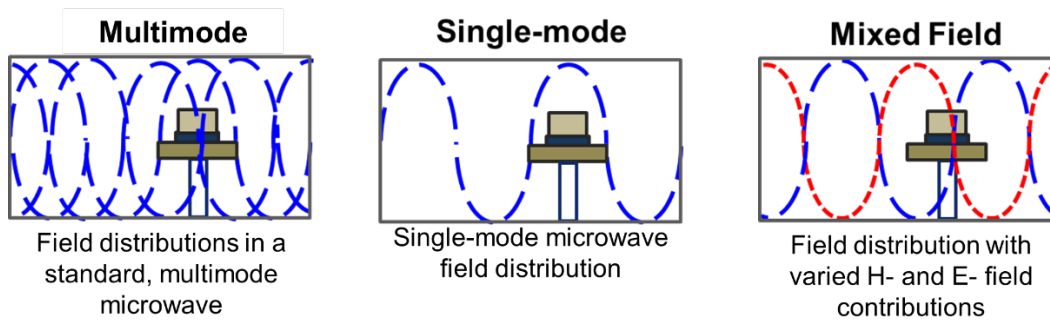


Fig. 2 Idealized field distributions in a multimode microwave (left), a single-mode microwave (center), and a mixed-field microwave (right)

1.2 Microwave-Susceptible Materials

The most well-known microwave absorber is water. This translates into rapid heating of food items in a kitchen microwave, as the water molecules are dipolar, and the water in the food oscillates from the microwave energy. Rapid heating due to oscillation also applies to microwave synthesis of ceramic nanoparticles, as the solutions being reacted are typically dipolar solutions. However, microwave sintering of ceramics has a different mechanism, as microwave-susceptible materials heat internally (inside-out) due to a moderate to high dielectric loss ($\tan \delta_e$).^{3,5-9} The magnitude of the dielectric loss of the material is directly related to the heating rate of the material.

The most significant drawback to microwave sintering is that it is not a universal method of sintering—only materials with a high dielectric loss will benefit from internal heating when exposed to microwave energy. Microwave-transparent materials do not couple well with microwaves, leading to slower heating rates or lack of heating. Typically, materials become more susceptible to microwaves as their temperature increases, indicating that radiant heat sources can assist the process.⁸ The common method used to circumvent this issue is to design a die or crucible that is susceptible to microwaves and place the material of interest into the die. In the microwave furnace, the susceptor will heat internally, and transfer of heat to the material will occur through contact between the susceptor and the sample.^{8,9} While increasing heating rates using susceptors is more effective than radiant heating techniques, it can lead to other processing challenges such as susceptor-sample contamination, thermal runaway, and decreased reproducibility.⁸

The most common external susceptor material is graphite, which has a $\tan \delta_e$ of approximately 0.4%. Commercial industries use graphite for sintering and hot pressing due to its lower cost and accessible tooling. Bhattacharya and Basak completed a review paper on microwave susceptors, describing several material options for susceptors.⁸ For example, magnetic ferrite materials (Fe_3O_4 , $\text{BaFe}_{12}\text{O}_{19}$, CuFe_2O_4) are typically highly responsive to 2.45-GHz microwave frequencies (both magnetic and electric components) with a $\tan \delta_e$ between 0.02% and 0.09%. Several microwave-susceptible materials of interest from Bhattacharya and Basak include silicon carbide (SiC), carbon fibers, and carbon black.⁸

1.3 Hypothesis

This research aims to further develop single-mode microwave sintering such that any material can be sintered to near full density. Currently, external microwave susceptors are relatively common. It is hypothesized that a microwave-absorbing material distributed through a microwave-transparent material will uniformly heat and sinter the material more efficiently than a radiant heating furnace. As a proof of concept, this work is conducted by using nickel ferrite (NiFe_2O_4) mixed into aluminum oxide (Al_2O_3) and pressed into pellets, as shown in Fig. 3.

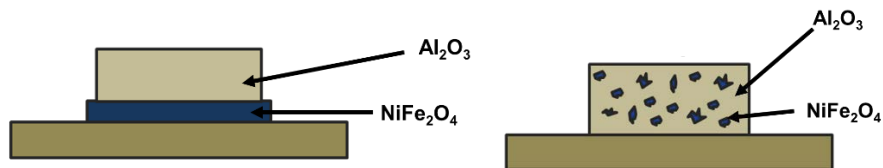


Fig. 3 Schematic of a hot plate susceptor, similar to what is currently done to sinter microwave-transparent materials (left) and schematic of the internal susceptor, NiFe_2O_4 , inside of an alumina compact (right).

A pellet is sintered to a maximum temperature and held for 1 h using the single-mode microwave method. Another pellet is heated by an air-fire furnace (radiant heating) to the average dwell temperature achieved in the microwave furnace for an hour. The two pellets are characterized by scanning electron microscopy (SEM) and Archimedes density methods.

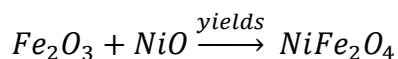
2. Experimental Procedures

2.1 Materials Selection Process

A series of experiments were conducted to determine which materials would be chosen for the proof-of-concept study. It was first decided to work with oxide ceramic materials (zirconium oxide [ZrO₂], Al₂O₃, NiFe₂O₄, and cobalt ferrite [CoFe₂O₄]), as they can be easily sintered in air. Initially, mixtures of ZrO₂/CoFe₂O₄ and ZrO₂/NiFe₂O₄ were sintered in air (air-fired), but these materials exhibited severe reaction of the components, leading to significant melting of the pellets inside the furnace with plasma formation. Al₂O₃/CoFe₂O₄ and Al₂O₃/NiFe₂O₄ were found to be more compatible combinations, as they did not react with each other and reached greater than 90% of theoretical density at high temperature. In the first set of microwave experiments, it was observed that the CoFe₂O₄ heated much more rapidly, and uncontrollably, leading to melting and fracture of the samples in the microwave furnace. The nickel ferrite material heated in a less dramatic fashion and was more controllable. The final combination of Al₂O₃ with 10% by weight nickel ferrite NiFe₂O₄ was selected for further experimentation.

2.2 Materials Preparation

The ferrite materials were synthesized via solid-state reaction of oxide components at high temperatures according to the following chemical equation:



All components were first dried in an air-fire furnace up to 1000 °C for 1 h to remove all adsorbed water. The iron oxide and nickel oxide were then prepared in stoichiometric amounts to yield a 20-g batch. The materials were ball milled in isopropanol with alumina milling media for ~72 h. The slurry was then decanted from the media and set on a stir plate to evaporate the alcohol by heating in a fume hood. After drying, the powder was gently crushed with a glass mortar and pestle. The crushed, mixed powder was loaded into a covered alumina crucible and air-

fired to 1100 °C for 1 h (10 °C/min heating rate) to obtain the final nickel ferrite phase, as confirmed by powder X-ray diffraction.

The individual nickel ferrite and alumina powders were weighed prior to mixing to yield a composite powder which contained 10% by weight of ferrite in alumina. The material was loaded into a Nalgene bottle with isopropanol and alumina milling media, and allowed to ball mill for approximately 24 h. The material was similarly dried and crushed as described previously. In order to remove any traces of Nalgene particles from milling, the powder was calcined at 450 °C for 1 h (5 °C/min heating rate).

After calcining, the powder was pressed into pellets at 24.3 MPa using a 13-mm stainless steel die. The pressed pellets were vacuum sealed into bags and cold isostatically pressed (CIP) up to 206 MPa for 30 s. These pellets were used for experimentation in the microwave and air-fire furnaces. Pure alumina and pure ferrite pellets were also prepared using a similar method to that described previously. The pure ferrite pellet was sintered in air at 1100 °C for 1 h and used as a plate susceptor to sinter the pure alumina pellet.

2.3 Single-Mode Microwave System

Figure 4 shows a schematic of the 2.45-GHz single-mode microwave system. The system includes a microwave generator and a wave guide. The power monitor measures the forward and reverse microwave power, which assists in determining how well the sample is coupling with the microwave energy. If the reverse power is greater than zero, it is assumed that the microwave power is being reflected back to the monitor and not being absorbed by the specimen in the chamber.

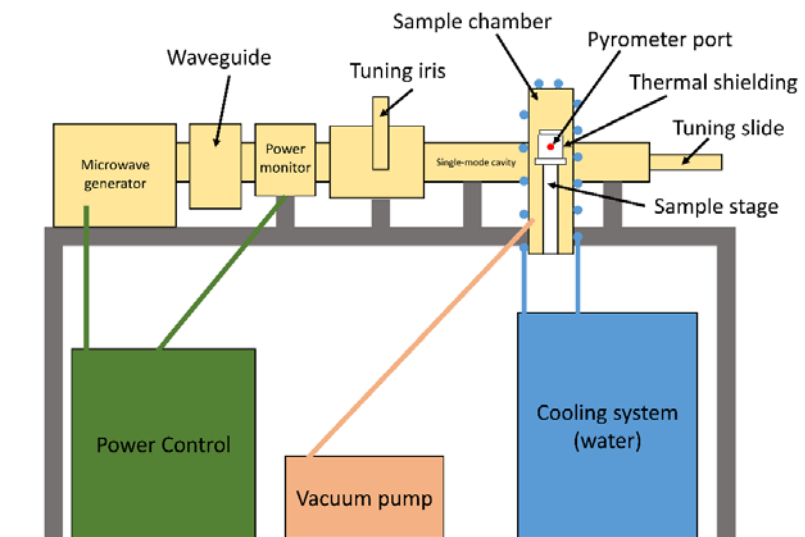


Fig. 4 Schematic of the 2.45-GHz single-mode microwave furnace

The tuning iris assists with coupling the microwave to the sample by shaping the microwave as it enters the cavity. The sample chamber is wrapped in copper tubing to mitigate heat and is connected to a water-to-water cooling system. The sample pellet is set inside refractory thermal shielding to limit radiant heat loss from the sample, as shown in Fig. 5. A small hole in the shielding and cavity act as a port for a two-color optical pyrometer, which measures temperatures ≥ 700 °C. The tuning slide at the end of the cavity lengthens or shortens the cavity to control the desired ratio of electric to magnetic field that is concentrated (i.e., a maximum) over the sample stage. A vacuum pump is also attached to the sample chamber to flush out air for experiments run in inert atmosphere.



Fig. 5 Alumina-ferrite composite (~13-mm diameter) set on refractory plate and the thermal shielding

The pellet was set on the refractory plate inside the thermal shielding and placed into the sample chamber. The sample was then aligned with the optical pyrometer by adjusting the stage height. Since the experimental samples were made of oxides, all microwave sintering was completed under ambient atmosphere. Four experiments were completed, as described in Table 1.

Table 1 List of experiments conducted as a proof of concept with relevant processing details; all specimens were held at temperature for 1 h

Experiment number	Microwave or air-fire furnace	Hold temperature (°C)	Heating rate (°C/min)	E/H ratio	Internal or external susceptor
1	Microwave	1236	NM	30/70	External (NiFe ₂ O ₄ plate)
2	Microwave	1070	~104	30/70	Internal (10% NiFe ₂ O ₄)
3	Air-fire	1070	10
4	Air-fire	1400	10

Notes: E/H = electric field to magnetic field ratio; and NM = not measured.

The two air-fired experiments were completed in an 8-inch box, CM Furnace under ambient atmosphere. Each alumina/ferrite pellet was placed on alumina beads inside of an alumina boat for the air-fire process. The beads allowed the pellet to shrink without being constrained by the surface of the boat.

2.4 Evaluation of Specimens

The density of the resulting parts from Experiments 2–4 was calculated by measuring the dry mass, the wet mass (specimen vacuum infiltrated with deionized water), and the wet suspended mass to obtain the bulk density. The density of the nickel ferrite powder was calculated by measuring the total volume of powder in a known mass via helium pycnometry. The theoretical density of the alumina/ferrite mixture was calculated as 4.13 g/cm^3 . The density of the alumina pellet from Experiment 1 was calculated by measuring the geometry before and after sintering and the mass of the specimen, as the pellet retained a cylindrical shape. The theoretical density of alumina was estimated as 3.98 g/cm^3 in the case of alumina on a ferrite susceptor plate. The green density for a composite pressed pellet prior to any heat treatment was calculated to be 59% of the theoretical density.

The sintered pellets were cross-sectioned and ground flat before mounting into a Leica TIC-3X for cross-sectional ion milling. The specimens were milled at 8 kV and 3 mA for approximately 6 h to produce a polished surface suitable for imaging. The specimens were imaged using a Hitachi field emission SEM in back-scatter mode.

3. Results and Discussion

Experiment 1 was the first microwave experiment conducted using a pure alumina pellet on top of a sintered NiFe_2O_4 plate as an external susceptor. The alumina sample reached an average temperature of $1236 \text{ }^\circ\text{C}$, where it was held for 1 h. The temperature did not increase beyond a maximum of $1274 \text{ }^\circ\text{C}$ due to plasma formation, which limited coupling and, therefore, heating. At the end of the hold time, the microwave power was turned off, and the sample was allowed to cool. After sintering, the geometric density of the sample was measured as 2.63 g/cm^3 , which was 66% of the theoretical density of pure alumina, as shown in Table 2. This was only approximately 8% greater density than the green density of 58% (for the green pellet of pure alumina).

Table 2 Bulk density and correlated percent of theoretical density of the completed experiments

Experiment number	Microwave or air-fire furnace	Hold temperature (°C)	Bulk density (g/cm³)	Percent of theoretical density
1	Microwave	1236	2.63 ^a	66%
2	Microwave	1070	3.33	81%
3	Air-fire	1070	3.00	73%
4	Air-fire	1400	3.88	94%

^a Density measured geometrically; all others measured by Archimedes method as previously described.

The shrinkage of the specimen was not uniform, as the majority of the shrinkage occurred on the surface closest to the nickel ferrite plate. Also, there appeared to be some discoloration on the surface of the alumina pellet next to the ferrite plate. This indicates that some iron or nickel may have diffused into the alumina, creating colored centers. Since the specimen reached a temperature greater than 1000 °C, the alumina pellet likely began coupling as a combined result of the microwave and the heat transfer from the ferrite susceptor plate.

Experiment 2 involved microwave sintering the alumina/ferrite composite material, which took approximately 10 min to reach a maximum temperature of 1130 °C. After the maximum temperature was reached, the power and tuning positions were held constant for 1 h, leading to an average temperature of 1070 °C experienced by the sample during that time. At the end of the hour, the power was turned off. The recovered sample appeared to be inhomogeneous, as slight color changes were identified on some of the surface regions. As in Experiment 1, the temperature did not increase beyond 1130 °C due to plasma formation and difficulties with coupling. The sample from Experiment 2 sintered to 81% of the theoretical density, significantly higher than that of Experiment 1 (which incorporated the external susceptor) despite reaching a lower hold temperature.

Figure 6 shows the measured temperature of the sample versus the microwave power for Experiments 1 and 2. Experiment 1 reached a higher temperature at lower microwave power, likely due to the more intense coupling of the ferrite susceptor plate with the microwave energy. In contrast, the sample in Experiment 2 required more energy to reach temperature due to the lower amount of susceptor material in the composite specimen. It is possible that increasing the concentration of the ferrite in the composite could reduce the energy requirement for the composite system.

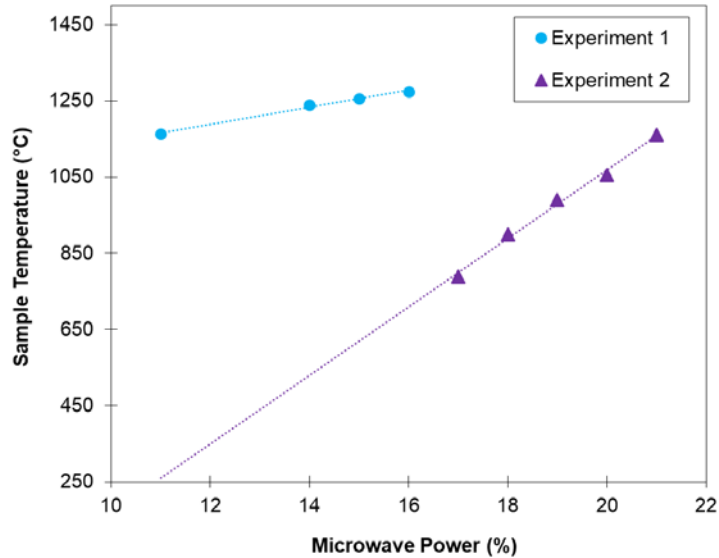


Fig. 6 Percent of microwave power from the 2-kW microwave generator versus observed sample temperature. Reflected microwave power is negligible as the sample absorbed the total input microwave energy.

To replicate the microwave sintering conditions in the air-fire furnace, Experiment 3 involved radiant heating of an alumina/ferrite pellet to 1070 °C at 10 °C/min and holding at temperature for 1 h. The sample also experienced a slight color change that was uniform throughout the part. The X-ray diffraction pattern did not indicate any development of a third phase. Rather, the pattern indicated a slight solubility of the nickel and iron into the alumina matrix. The density was calculated as 3.00 g/cm³, approximately 73% of the theoretical density of the mixture. The air-fired sample from Experiment 3 had a lower density than Experiment 2. The main difference between the two experiments was the drastic change in heating rate (10 °C/min in the air-fire furnace vs. 104 °C/min in the microwave furnace), which could be equated to fast-firing (inserting a sample into the furnace at temperature). However, Brosnan et al. indicated that simple fast-firing was not necessarily the conclusion, as the observed grain size and density trajectory were independent of the heating source.⁷ Furthermore, Brosnan et al. used SiC powder as a susceptor material.

Figure 7 shows back-scatter SEM images of the samples from Experiments 3 and 2. The microstructures were very similar in terms of the grain size of the alumina phase (darker) and the ferrite phase (brighter), similar to Brosnan et al.⁷ Visual observation might also be misleading, as it appeared that the samples had a similar level of porosity (black patches), but the density values indicated that the air-fired specimens had approximately 8% more porosity as indicated by the lower theoretical density.

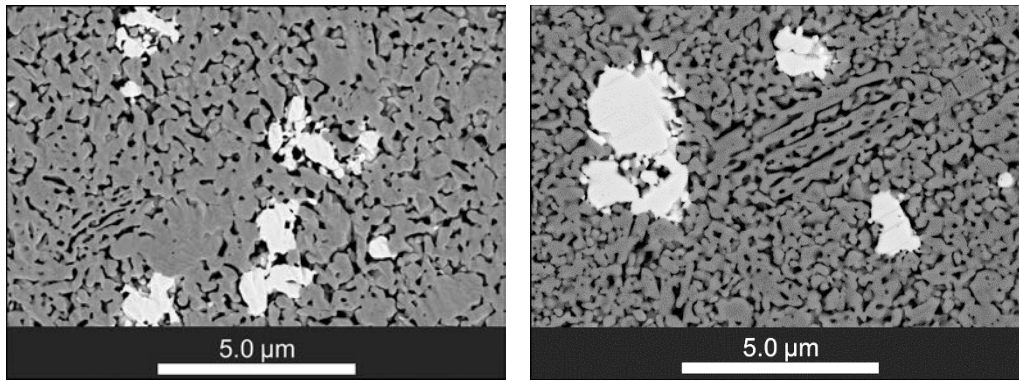


Fig. 7 SEM image of the air-fired alumina/ferrite mixture held at 1070 °C for 1 h from Experiment 3 (left); SEM image of the microwave-sintered alumina/ferrite mixture held at 1070 °C for 1 h from Experiment 2 (right).

In Experiment 4, an alumina/ferrite sample was air-fired at 1400 °C for 1 h and reached approximately 94% of the theoretical density of the mixture. This experiment was carried out to show how the microstructure could evolve should the material experience more densification. Figure 8 shows a SEM image of the sample in which significant porosity surrounds the ferrite grains and alumina triple points. The overall grain size was much larger than in Fig. 7, which is at a higher magnification, due to the higher sintering temperature.

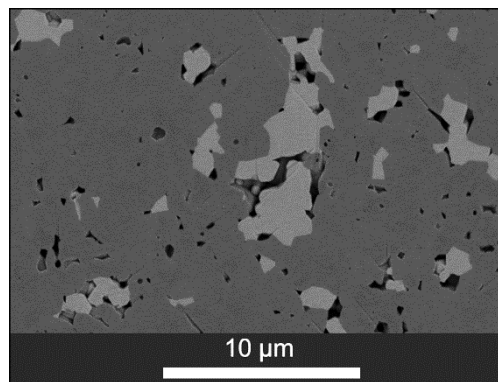


Fig. 8 SEM image of the air-fired alumina/ferrite mixture held at 1400 °C for 1 h in Experiment 2

4. Conclusion

Four sintering experiments were completed to evaluate the effectiveness of internal microwave susceptors and improve the densification rate of microwave-transparent materials. A microwave sintering experiment using a microwave-susceptible nickel ferrite plate in contact with an alumina pellet yielded a density 8% greater than the original green density. The susceptor plate was in contact with only the bottom surface of the alumina pellet, leading to uneven heating and a density gradient

through the thickness of the sample. This could be addressed by adding an additional susceptor plate in contact with the top of the alumina sample. However, designing the susceptor geometry for complex shaped parts (i.e., to support additive manufacturing of ceramics) will be challenging. The internal susceptor method increased the density by 22%, and at a lower temperature. However, the resulting sample appeared to be inhomogeneous

The microwave-sintered alumina/ferrite composite exhibited a higher density and a similar microstructure when compared to a conventionally air-fired sample held at the same average temperature. The microwave-sintered sample reached the hold temperature a full order of magnitude faster than the air-fired sample, potentially leading to higher densification kinetics and a higher-density product.

While this work was only a proof-of-concept study, improvement in density has been demonstrated by incorporating an internal susceptor material into a microwave-transparent material. The internal susceptor heated preferentially within the alumina matrix, leading to densification of the part. The internal susceptor technique could be useful for sintering additively manufactured parts. The literature has indicated that faster sintering rates and finer grain sizes can be achieved through microwave sintering, drastically improving the mechanical properties of ceramics.

This work will continue by expanding material testing to include silicon carbide, boron carbide, and titanium diboride. Silicon carbide has proven to be microwave-susceptible, though some chemistries are more effective than others. Graphite and carbon black are well-known microwave susceptors and materials that are commonly used as sintering aids in boron carbide and silicon carbide during conventional hot pressing of armor ceramics. Future work will focus on these materials systems in order to obtain finer grain sizes and improved mechanical properties. Expected challenges include managing or eliminating plasma formation to improve coupling and achieve higher temperatures, and establishing further process control over the single-mode microwave system.

5. References

1. Slutz D, Keshavan M, Griffo A. Microwave sintering. United States patent 20070151769A1. 2005.
2. Slutz D, Keshavan M, Griffo A. Cutting elements formed from microwave sintering. United States patent GB2435476B. 2005.
3. Cheng JP, Agrawal DK, Komarneni S, Mathis M, Roy R. Microwave processing of WC-Co composites and ferroic titanates. *Materials Research Innovations*. 1997;1: 44–52.
4. Oghbaei M, Mirzaee O. Microwave versus conventional sintering: a review of fundamentals, advantages and applications. *Journal of Alloys and Compounds*. 2010;494:175–189.
5. Vaidhyanathan B, Singh A, Agrawal D, Shrouf T, Roy R, Ganguly S. Microwave effects in lead zirconium titanate synthesis: enhanced kinetics and changed mechanisms. *Journal of the American Ceramic Society*. 2001;84:1197–1202.
6. Roy R, Peelamedu R, Hurtt L, Cheng J, Agrawal D. Definitive experimental evidence for microwave effects: radically new effects of separated E and H fields, such as decrystallization of oxides in seconds. *Materials Research Innovations*. 2002;6:128–140.
7. Brosnan K, Messing G, Agrawal D. Microwave sintering of alumina at 2.45 GHz. *Journal of the American Ceramic Society*. 2003;86:1307–1312.
8. Bhattacharya M, Basak T. A review on the susceptor assisted microwave processing of materials. *Energy*. 2016;97:306–338.
9. Bhattacharya M, Basak T. Susceptor-assisted enhanced microwave processing of ceramics – a review. *Critical Reviews in Solid State and Materials Sciences*. 2017;42:433–469.
10. Croquesel J, Carry CP, Chaix J-M, Bouvard D, Saunier S. Direct microwave sintering of alumina in a single mode cavity: magnesium doping effects. *Journal of the European Ceramic Society*. 2018;38:1841–1845.
11. Pavlacka R, Brennan C, Blair V, Brennan R, Fountzoulas C, Cheng J, Agrawal D. Single-mode microwave sintering of Er:Al₂O₃. In: Mahmoud MM, Bhalla A, Bansal NP, Singh JP, Castro RHR, Manjooran NJ, Pickrel G, Johnson S, Brennecke G, Singh G, Zhu D. *Processing and properties of advanced*

ceramics and composites VII. Hoboken (NJ): John Wiley & Sons, Inc.; 2015. pp. 1–11.

12. Cheng J, Roy R, Agrawal D. Radically different effects on materials by separated microwave electric and magnetic fields. *Materials Research Innovations*. 2002;5:170–177.

List of Symbols, Abbreviations, and Acronyms

Al_2O_3	aluminum oxide
ARL	US Army Research Laboratory
CIP	cold isostatic pressing
CoFe_2O_4	cobalt ferrite
NiFe_2O_4	nickel ferrite
SEM	scanning electron microscopy and/or scanning electron microscope
SiC	silicon carbide
WC-Co	cobalt-cemented tungsten carbide
ZrO_2	zirconium oxide

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