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Advanced Sintering of Nano-Ceramic Materials

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1. Introduction

In the past few years, the use of ceramic materials has significantly increased in various applications due to the unique characteristics of these materials in comparison with metals and polymers. The advantageous properties of ceramic materials are hardness, rigidity, abrasive toughness and low density. Ceramics are a class of materials broadly defined as "inorganic, nonmetallic solids". They have the largest range of functions of all known materials. The last decades have seen the development of the enormous potential of functional ceramics based on unique dielectric, ferroelectric, piezoelectric, pyroelectric, ferromagnetic, magnetoresistive, ionical, electronical, superconducting, electrooptical, and gas-sensing properties. Similar scientific developments also have taken place in structural ceramics. Thermal, chemical, and mechanical stability of many oxide and nonoxide compounds laid the foundation for improved processing, which led to an improved level of microstructure design and defect control. This in turn resulted in never-before-seen improvements in mechanical performance and in the reliability of the properties of components and devices.

In addition, superior combinations of thermal, insulating, and mechanical properties have become the basis of huge applications in the packaging of microelectronics and power semiconductors. Therefore, ceramic materials have now become the cornerstone of such advanced technologies as energy transformation, storage and supply, information technology, transportation systems, medical technology, and manufacturing technology. In addition to these trends, present-day environmental regulations and awareness and the recycling of materials will affect the use of materials and require less expensive production processes. Following technological trends, the needs for future basic research in the field of ceramics can be divided into four major areas:

(1) materials and materials properties research in order to widen the area's scope and match its needs for future applications, (2) research to increase the knowledge of economical and

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ecological production processes for materials, components, and devices, (3) miniaturization and integration, and (4) modeling and numerical simulation, which would complement or even act as a substitute for present areas of experimental work, thus not only directing research to defined questions, but also reducing practical work and time periods typically combined with product development.

Nanocrystalline ceramic materials have been the subject of interests and focus of research programs around the world for the past two decades owing to the expectations that the mechanical behavior may improve significantly when grain sizes reduce to nanometer scale. However, although numerous technologies are available for making nanosized ceramic powders, obtaining true nanocrystalline ceramic (average grain size <100 nm) has been a great challenge due to the difficulties of controlling grain growth during sintering. Thus, the use of conventional methods of powder consolidation often result in grain growth in the compact or surface contamination due to the high temperatures and long sintering duration involved. It is therefore essential to minimize grain growth through careful control of the consolidation parameters, particularly sintering temperature and time. Evaluation of the mechanical properties of nanocrystalline ceramic materials is also difficult because there are little published data that are based on specimens with truly nanoscale grain sizes.

In this chapter, the challenges and results of sintering nanocrystalline ceramic powders will be examined as well as the various technologies for producing nanosized ceramic powders. The key challenge to the production of bulk nanocrystalline ceramic materials is to control the rapid grain growth during the early stage of sintering. This chapter provides an overview of the development of nanocrystalline ceramic materials. The review will first summarize different methods of advanced sintering of nanosized ceramic powders. The review of the advanced sintering and consolidation of the nanosized ceramic powders will emphasize the challenges and the progress toward achieving nanoscale grain sizes, or grain sizes that are as fine as possible, at sintered states. In the last section of this review, focusing on the high frequency induction heat sintering of nanosized ceramic powders will be given in details and summarized.

2. Conventional sintering process

Dense nanostructured ceramic materials are usually obtained by pressing and conventional sintering of nanopowders using pressure assisted methods, such as hot pressing, hot isostatic pressing, sinter forging, etc. (M.J. Mayo, 1997; J.R. Groza, 1999; Dj. Veljovic et, al., 2007). The high sintering temperatures and long sintering times required for the consolidation of ceramic powders often result in extreme grain coarsening and decomposition of the ceramic, which is characteristic for conventional sintering methods and results in the deterioration of the mechanical properties of ceramics (Y.W. Gua et al., 2004 & C.Y. Tang et al., 2009). Hot pressing of some ceramic materials was found to allow the occurrence of densification at temperatures much lower than during conventional sintering (R. Halouani et al., 1994 & Dj. Veljovic et al., 2009). The advantages of the hot pressing technique are the enhancement of the densification kinetics and the limiting of grain growth, while the disadvantages are the limited geometry of the end product and the expensive equipment required. Furthermore, in conventional HP techniques, the powder container is typically heated by radiation from the enclosing furnace through external heating elements and convection of inert gases if applicable. Therefore, the sample is heated

as a consequence of the heat transfer occurring by conduction from the external surface of the container to the powders. The resulting heating rate is then typically slow and the process can last hours. In addition, a lot of heat is wasted as the whole volume of space is heated and the compact indirectly receives heat from the hot environment.

3. Advanced sintering process

Consolidation of nanocrystalline powders is a very difficult problem. A peculiarity of sintering nanocrystalline powders is competition between the processes of densification and microstructure coarsening, which occur in parallel. In order to consolidate a material with a density close to theoretical and a grain size as small as possible, various techniques have been developed that accelerate the former and decelerate the latter factors. Of these, methods involving fast heating, high pressure, and addition of various agents that accelerate shrinkage and inhibit grain growth are the best known. To overcome the problem of grain growth, unconventional sintering and densification techniques have been proposed. Advanced sintering was found to show great potential in ceramics processing (S. Vijayan & H. Varma, 2002). These include the use of grain growth inhibitors in solid solution or forming discrete second phases, high-pressure densification, spark-plasma sintering and related techniques, shock densification, high-frequency induction heating and magnetic pulse compaction (Allen et al., 1996; Kim and Khalil, 2006; Godlinski et al., 2002; Krell et al., 2003; Jiang et al., 2007).

3.1 Microwave sintering

Microwave sintering of ceramics in general has been known for the past three decades. It has several advantages with regard to processing like being rapid and possibility of selective heating, imparting improved properties to the processed materials by way of inhibiting grain growth in addition to reducing the processing time and energy required (Clark D & Sutton WH, 1996; Katz JD, 2005; Agarwal DK, 2005). Use of microwave technology in material science and processing is not rather new. The areas where this technology has been applied include: process control, drying of ceramic sanitary wares, calcination, and decomposition of gaseous species by microwave plasma, powder synthesis, and sintering (D. Agrawal & Sohn, 2006). Microwave processing of materials was mostly limited until 2000 to ceramics, semiconductors, inorganic and polymeric materials. There was a misconception between researchers that all metals reflect microwave or cause plasma formation, and hence cannot be heated, except exhibiting surface heating due to limited penetration of the microwave radiation. The researchers did not notice that this relation is valid only for sintered or bulk metals at room temperature, and not for powdered metals and/or at higher temperatures (D. Agrawal & Sohn, 2006). No wit has been found that the microwave sintering can also be applied as efficiently and effectively to powdered metals as to many ceramics.

This technique provides a series of benefits, such as great microstructure control, no limit of the geometry of the product, improved mechanical properties of the materials and reduced manufacturing costs due to energy savings, lower temperatures of sintering and shorter processing times. Microwave energy is a form of electromagnetic energy with the frequency range of 300MHz to 300 GHz. Microwave heating is a process in which the materials couple

with microwaves, absorb the electromagnetic energy volumetrically, and transform into heat. This is different from conventional methods where heat is transferred between objects by the mechanisms of conduction, radiation and convection. In conventional heating, as mentioned before, the material's surface is first heated followed by the heat moving inward. This means that there is a temperature gradient from the surface to the inside. However, microwave heating generates heat within the material first and then heats the entire volume (P. Yadoji et al., 2003). This heating mechanism is advantageous due to the following facts: enhanced diffusion processes, reduced energy consumption, very rapid heating rates and considerably reduced processing times, decreased sintering temperatures, improved physical and mechanical properties, simplicity, unique properties, and lower environmental hazards. These are features that have not been observed in conventional processes (P. Yadoji et al., 2003; D. Agrawal, 1999; D.E. Clark & D.C. Folz, J.K., 2008; C. Leonelli, P. et al., 2008; R.R. Menezes, 2007). The microwave furnace is shown in Figure 1.

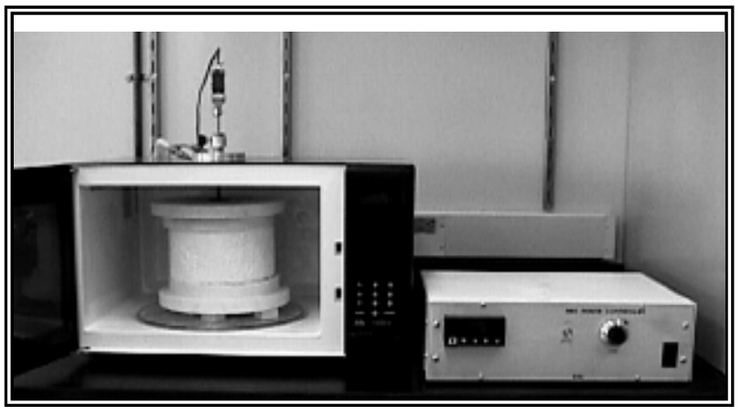


Fig. 1. Microwave furnace with thermal pod, thermocouple, and controller.

In addition to a microwave furnace, the critical components for microwave sintering include an insulation box and susceptors. The insulation box consists of a small chamber fabricated from low-density rigid insulation board. Low density and very low dielectric loss are required for the box to make it microwave transparent. Microwaves pass through the material with little interaction, allowing the contents to heat. The box, in essence, acts as an oven within the microwave chamber or applicator, as it allows microwaves to pass though but contains the heat generated by the contents. Many ceramic materials do not absorb microwaves (2.45 GHz) well at room temperature (Committee on Microwave, 1994). Susceptors are useful for initial heating of these ceramics. Susceptors are made of a material that absorbs microwaves at room temperature and act as heating elements, which "boost" the temperature until the dielectric loss in the ceramic is high enough that the ceramic couples directly with the field. For example, using silicon carbide susceptors, zirconia will heat primarily by radiation from the SiC, until it reaches approximately 600°C, whereby the zirconia couples preferentially and heats volumetrically.

Microwave sintering of cemented carbides like WC–Co also has been investigated since 1991 after the pioneering work of Cheng (Cheng J, 1991; Cheng JP et al., 1997; Breval E et al., 2005) and thereafter by Porada (Gerdes T & Porada MW, 1994; Rodinger K et al., 1998; Kolaska H et al., 2000). Breval et al. (Breval E et al., 2005) investigated on the microwave

sintering of 0.1–1 μm sized WC particles with cobalt as the binder and compared the results with conventional sintering of the same powders. They reported that the microwave sintered sample hardly exhibits any growth and the cobalt phase does not reveal any dissolution of tungsten whereas in the conventionally sintered sample, nearly 20% of W had dissolved in the cobalt binder phase. They found that the microwave sintered sample always showed improved mechanical properties when compared to the conventionally sintered one. Porada and her group showed that the microwave reaction sintering of W, C and Co powders yielded sintered WC–6Co compacts with fine and uniform microstructure (with an average grain size of 0.6 lm) which exhibited a 10% increase in hardness values in comparison to tools made by a conventional route (Gerdes T & Porada MW, 1994; Rodinger K et al., 1998; Kolaska H et al., 2000). Recently, microwave post-treatment of WC–Co cutting tools was also investigated by Ramkumar et al. Ramkumar J et al., 2002 & Aravindan S et al., 2005). These authors reported that a favorable response was obtained on microwave treatment of cemented WC drill inserts and the hardness had increased from 1372–1525 to 1700–1900 kg/mm^2 through a microwave treatment.

3.2 Spark plasma sintering

A spark sintering method was investigated and patented in the 1960s and used to compact metal powders, but due to high equipment cost and low sintering efficiency it was not put to wider use (Inoue, K. (US Patent NO. 3 241 956). The concept was further developed during the mid 1980s to the early 1990s, and a new generation of sintering apparatus appeared named Plasma Activated Sintering (abbreviated PAS) and Spark Plasma Sintering (abbreviated SPS). Common to these systems is the use of pulsed direct current to heat the specimens. These sintering techniques currently attract growing attention among productions engineers as well as materials researchers. Whether plasma is generated has not been confirmed yet, especially when non-conduction ceramic powders are compacted. It has, however, been experimentally verified that densification is enhanced by the use of a pulsed DC current or field (Mishra et al., 1998). This family of techniques is in academia also named as pulsed electric current sintering (PECS) (Yoshimura et al., 1998; Murayama, 1997; Zhou et al., 2000) or electric pulse assisted consolidation (EPAC) (Mishra et al., 2000). SPS allows compaction of ceramic and metal powders at low temperature and in short time (within minutes).

The basic configuration of a SPS unit is shown in Figure 2. It consists of a uniaxial pressure device, where the water-cooled punches also serve as electrodes, a water-cooled reaction chamber that can be evacuated, a pulsed DC generator, pressure-, position- and temperature-regulating systems. Spark Plasma Sintering resembles the hot pressing process in several respects, i.e. the precursor powder (green body) is loaded in a die, and a uniaxial pressure is applied during sintering process. However, instead of using an external heating source, a pulsed direct current is allowed to pass through the electrically conducting pressure die and, in appropriate cases, also through the sample. This implies that the die also acts as a heating source and that the sample is heated from both outside and inside. The use of a pulsed direct current also implies that the samples are exposed to a pulsed electric field during the sintering process. In the SPS method, the powder sample in a graphite die is gradually pressed in a vacuum, and heated by a pulse current (Joule heating). The sintering is considered to proceed very quickly due to the spark plasma induced by the large pulse

current. This can be attributed to the in situ particle surface activation and purification by the spark plasma generated during the process. Therefore, heat and mass transfer between the particles induced by electric current can be rapidly accomplished (R. Chaim et al., 2007; H. Borodianska et al., 2008; O. Vasylkiv et al., 2008; H. Borodianska et al., 2009). The very short duration and relatively low homologous temperature involved in the technique make it very attractive for densification and preservation of the nanocrystalline character in ceramics.

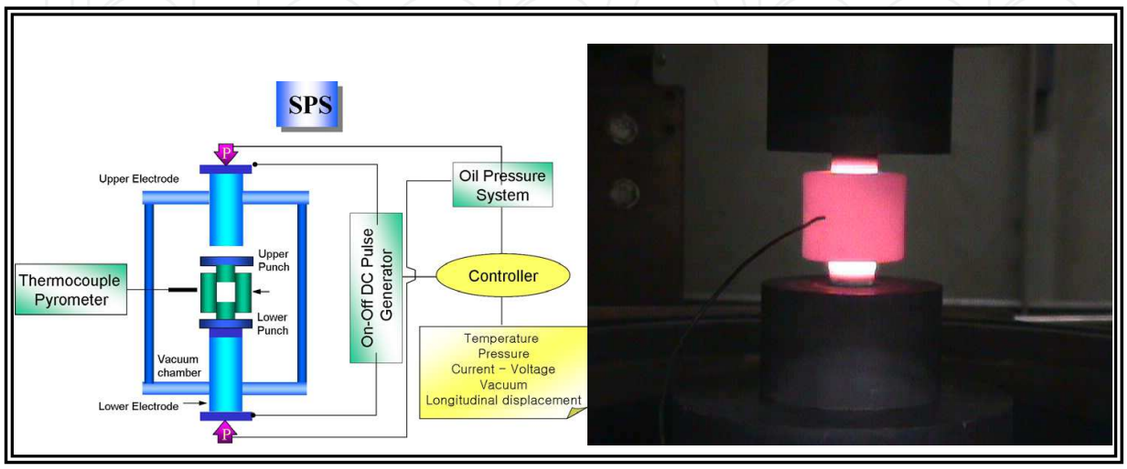


Fig. 2. Basic configuration of a typical SPS system and photo of the heated die.

Numerous experimental investigations point to the possibility of using SPS to consolidate parts to nearly full density while retaining the fine grain size and phase homogeneity composites (P. Angerer, et al., 2004; K. Kakegawa et al., 2003; K.A. Khor et al., 2004). This property of SPS is of undoubted significance in the case of manufacture of bulk nanostructured parts, for which the control of grain growth is one of the major problems (H. Borodianska et al., 2008; O. Vasylkiv et al., 2008; H. Borodianska et al., 2009). The formation of plasma at particle contacts makes it possible to obtain a fine-grained structure commensurable with the initial powder particle size. However, at the same time the grain-boundary framework in SPS-derived nanoceramics is often underdeveloped (H. Borodianska et al., 2009). The enhanced kinetics of different thermally activated processes where SPS was used, such as densification (Z.A. Munir et al., 2003; M. Nygren & Z. Shen, 2003; O. Vasylikiv et al., 2009; K. Morita et al., 2008), reactive sintering (W.W. Wu et al., 2007; J. Zhang et al., 2007; R. Licheri et al., 2008; J.G. Santanach et al., 2009), joining (Y.J. Wu, et al., 2003; W. Liu & M. Naka, 2003; C. Elissalde et al., 2007), liquid and solid state crystal growth (M. Omori, 2000; J.K. Park, 2006), raised questions whether the atomistic mechanisms active by conventional heating change due to the nature of the SPS process. In this respect, enhanced densification kinetics observed in YAG ($Y_3Al_5O_{12}$), was analyzed in terms of particle surface softening due to the plasma (R. Chaim et al., 2006). Such a behavior originated most probably from the extremely high creep resistance of YAG prohibiting plastic deformation, and its high electrical resistance enhancing charging and discharge at the particle surfaces. Therefore, densification of conducting or semiconducting ceramics by SPS may shed further light on the interrelations between the ceramic mechanical and electrical properties and its densification behavior by SPS. So, SPS is most promising and

has already proved successful in consolidation of various nanoceramics and composites (P. Angerer, et al., 2004; K. Kakegawa et al., 2003; K.A. Khor et al., 2004). SPS is widely used nowadays as it offers the possibility of performing a rapid consolidation of difficult-to-sinter ceramic and ceramic composites at reduced temperatures.

3.3 High frequency induction heat sintering

The novel technique of high-frequency induction heat sintering (HFIHS) has been shown to be an effective sintering method that can successfully consolidate ceramics and metallic powders to near theoretical density. The (HFIHS) process is a sintering method for the rapid sintering of a nanostructured hard metal in a high-temperature exposure along with pressure application. It is similar to hot pressing, which is carried out in a graphite die, but heating is accomplished by a source of high frequency electricity to drive a large alternating current through a coil. This coil is known as the work coil. The passage of current through this coil generates a very intense and rapidly changing magnetic field in the space within the work coil. The workpiece to be heated is placed within this intense alternating magnetic field. The alternating magnetic field induces a current flow in the conductive workpiece.

The basic configuration of a HFIHS unit is shown in Figure 3. It consists of a uniaxial pressure device, a graphite die (outside diameter, 45 mm; inside diameter, 20 mm; height, 40 mm). A water-cooled reaction chamber that can be evacuated, an induced current (frequency of about 50 kHz) pressure-, position- and temperature-regulating systems are also presented. HFIHS resembles the hot pressing process in several respects, *i.e.*, the precursor powder is loaded in a die, and uniaxial pressure is applied during the sintering process. However, instead of using an external heating source, an intense magnetic field is applied through the electrically conducting pressure die and, in some cases, also through the sample. Thus, the die also acts as a heating source, and the sample is heated from both

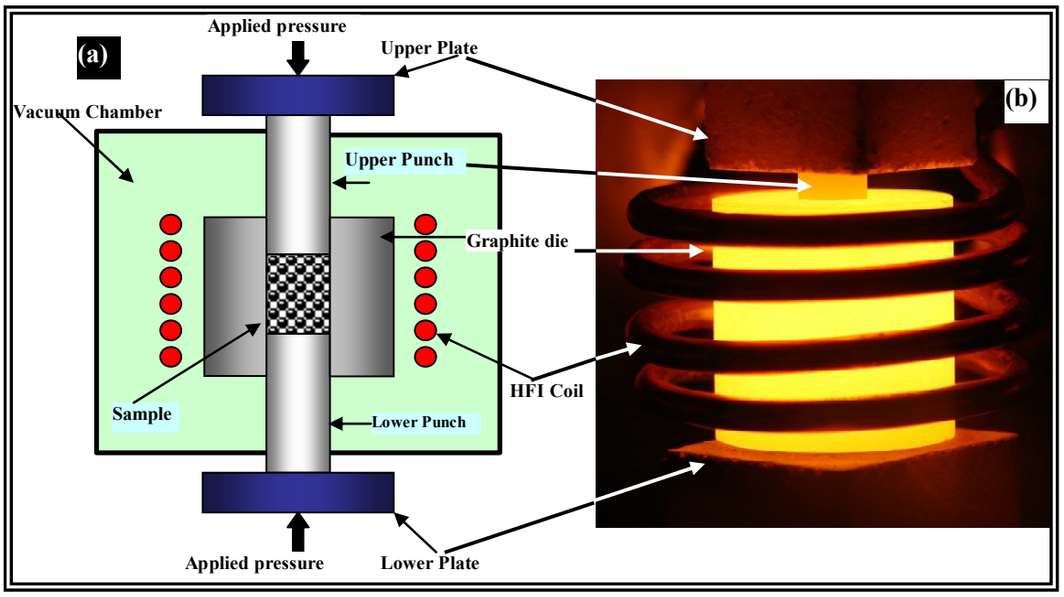


Fig. 3. (a) Schematic diagram of high-frequency induction heated sintering apparatus, (b) Photo of the heated die.

the outside and inside. Temperatures can be measured using a pyrometer focused on the surface of the graphite die. The system is first evacuated to a vacuum level of 1×10^{-3} Torr, and uniaxial pressure is applied. An induced current is then activated and maintained until densification, indicating the occurrence of sintering and the concomitant shrinkage of the sample, is observed. Sample shrinkage is measured by a linear gauge that measures the vertical displacement. The typical parameters for the process are presented in Table 1, and the four major stages of the HFIHS and densification processes are shown in Fig. 4.

Parameter	Applied value	Parameter	Applied value
Vacuum level	1×10^{-3} Torr	Applied pressure	10 - 300 MPa
Heating rate	100 - 1200 °C/min	Cooling rate	500 °C/min
Total power capacity	15 kW	Output of total power	0 - 100%
Resistance heating frequency	50 kHz	Duration time	~10 min

Table 1. Processing conditions of high-frequency induction heated sintering process

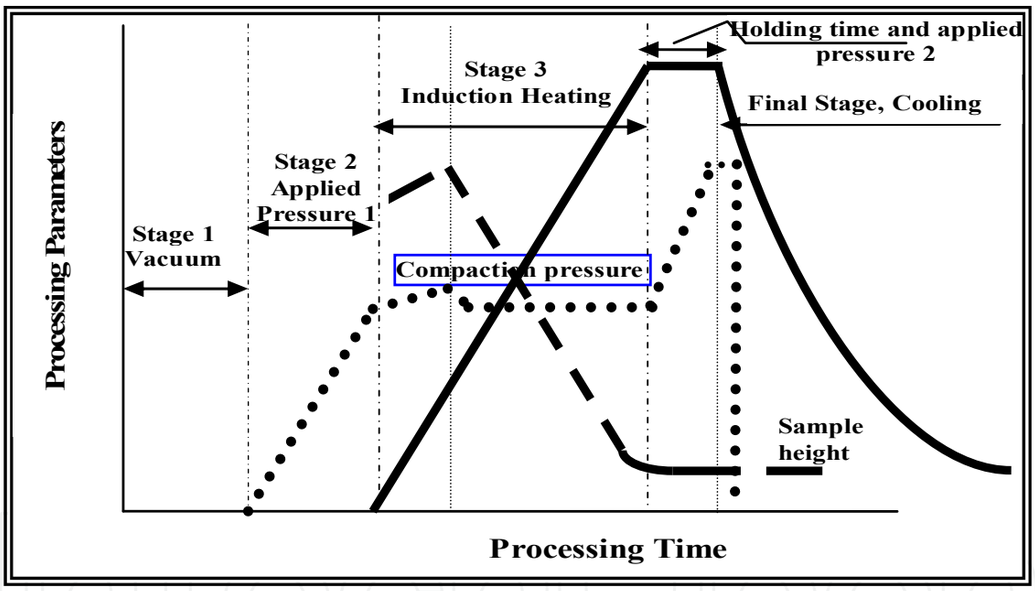


Fig. 4. The four major stages of sintering process in the HFIHS apparatus.

Induction heating has many advantages over competitive techniques, such as radiant or convection heat and laser technologies. This process is a non-contact technique, which provides localized heating through custom-designed coils. Since it is non-contact, and the heat is transferred to the product via electromagnetic waves, the heating process does not contaminate the material while being heated. The process is energy efficient process converts up to 80% of the expended energy into useful heat to save costs. It allows the right amount of heat to be applied exactly where it is needed for an exact period of time, ensuring controlled, accurate performance, increased production and reduced distortion.

Considerable research has been performed on using the novel technique of HFIHS (Khalil et al., 2006, 2007, 2010, 2011, 2012). The HFIHS process involves the rapid sintering of a

nanostructured hard metal in a very short time with high-temperature exposure and the application of pressure. This process is advantageous because it allows for rapid densification to near the theoretical density of the associated materials and inhibits grain growth in nanostructured materials. Another important reported aspect of the HFIHS process is the role of rapid heat transfer to the product via electromagnetic waves. In previous papers HFIHS (Khalil et al., 2006, 2007a, 2007b, 2007c), the authors have reported the investigation of the consolidation and mechanical properties of different nanostructured ceramic materials by HFIHS. The grain size of the sintered material was greater than 100 nanometers. Furthermore, the specific microscopic effects of HFIHS were not determined.

Khalil and S. W. Kim (Khalil & S. W. Kim, 2007) have studied sintering of Al_2O_3-8YSZ by HFIHS. They found that, HFIHS was effective in the preparation of fine-grained, nearly fully dense of Al_2O_3-8YSZ ceramics from the powder with a smaller particle size by optimizing the overall processing parameters. The samples were densified by heating to a sintering temperature in the range of 1300 to 1500°C, and then fast cooled to 500°C within short time. The density of the samples kept increasing with the rising of the sintering temperature; on the other hand sintering pressure has a relatively small influence on the density. For these composites, a relative density of more than 99% theoretical density was achieved after sintering at 1400°C. Low density was found when a higher heating rate, 700**°C/**min, was applied during the HFIHS process. Microstructure inhomogeneity, where the edge was denser than the inside of the sample, appeared with a high heating rate. A difference in temperature between the surface and the center of the sample exists, and it depends on the heating rate. When the heating rate was 200**°C/**min, the inside could be sintered almost as dense as the edge of the sample. Al_2O_3–(ZrO_2+ 8%mol Y_2O_3) nanopowders with 20 vol% – (ZrO_2+ 8%mol Y_2O_3) were consolidated very rapidly to full density using high frequency induction heating sintering (HFIHS).

The variations of shrinkage displacement and temperature with time for various maximum sintering temperatures under a pressure of 60 MPa are shown in Figure 5. In all cases, the application of the current and subsequent increase in temperature resulted in initial thermal expansion followed by shrinkage due to consolidation. The onset of shrinkage occurred at temperatures in the range of 600 to 800°C for all samples due to rearrangement of the powders as well as plastic deformations. As the temperature increased, the shrinkage displacement increased gradually. The rate of shrinkage decreased as a temperature of the maximum sintering temperature was reached. It is clear that, the rate of shrinkage displacement became zero when the maximum sintering temperature was reached. At a temperature of 1400°C, the specimen attained minimum height (maximum shrinkage) before reaching the maximum sintering temperature. Although, the maximum sintering temperature was reached at 1500°C, there was no more shrinkage beyond 1400°C. It is clear from these Figures that, the maximum sintering temperature with respect to maximum shrinkage was 1400°C.

Figures 6 and 7 show microstructures of the samples sintered at a heating rate of 200 and 700°C/min, respectively. In general, sintered samples with higher relative densities exhibit greater mechanical properties. However, there is also an influence of microstructural uniformity on mechanical properties. Figure 6 (a) to (d) shows various SEM micrographs of fracture surfaces of the samples. The microstructure seems to be like a green compact for the 1300**°C** sample because the sintering temperature was too low for sintering. In the case of

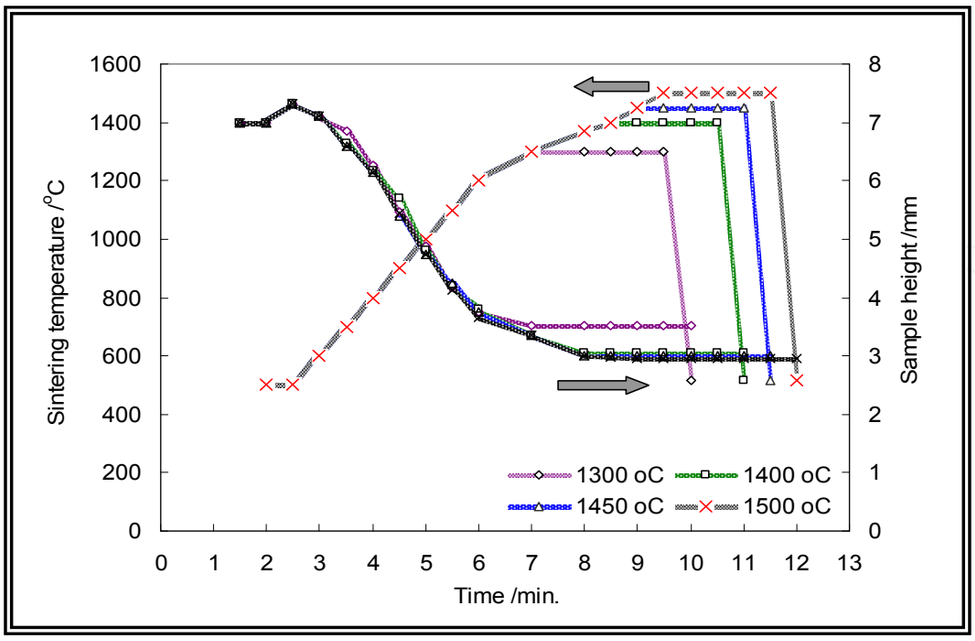


Fig. 5. Variations of temperatures and shrinkage displacements vs. heating time at various maximum sintering temperatures.

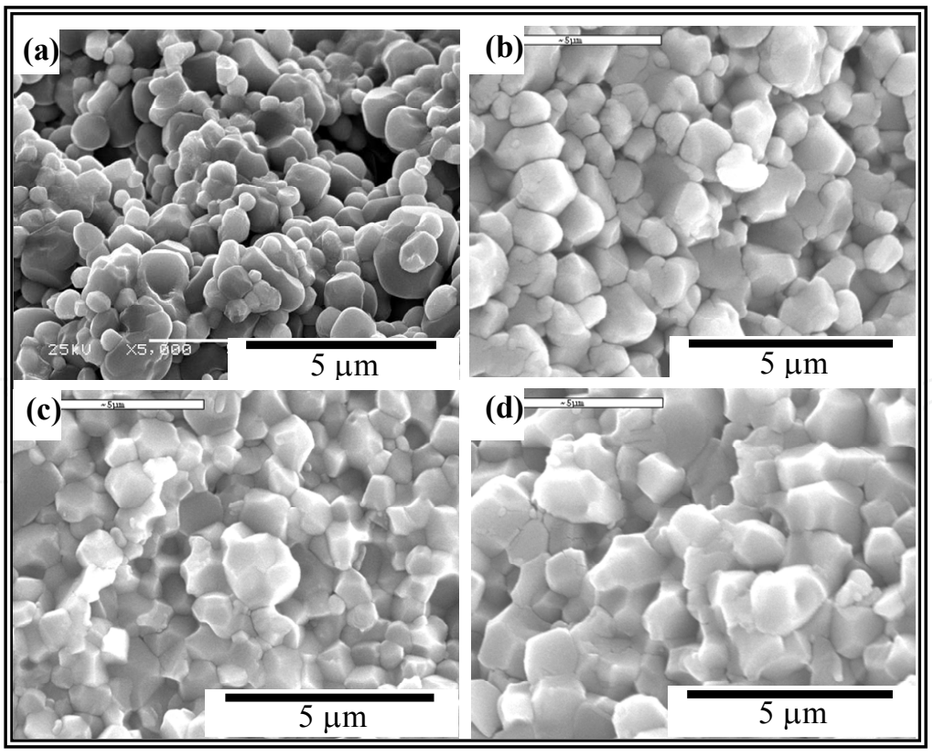


Fig. 6. Effect of sintering temperatures on Microstructure at 200 °C/min heating rate (a) 1300 °C, (b) 1400 °C, (c) 1450 °C, (d) 1500 °C.

Figure 6 (a), there exist a number of closed pores, entrapped in sample grains. Samples sintered at temperatures from 1400**°C** to 1450**°C**, showed highly homogeneous microstructures without agglomerates. These provided better densification, less porosity in the sample and no abnormally grown alumina grains. The intragranular fracture mode was dominant during fracture, indicating the presence of stiff grain-boundaries. This is clear in Figure 6 (c). At temperature 1500**°C**, Figure 6 (d), the grain size rapidly increased due to a high sintering temperature. Abnormal grains appeared only when the powder was sintered for a long sintering time (due to a lower heating rate, 200°C/min) and a high sintering temperature (1500°C).

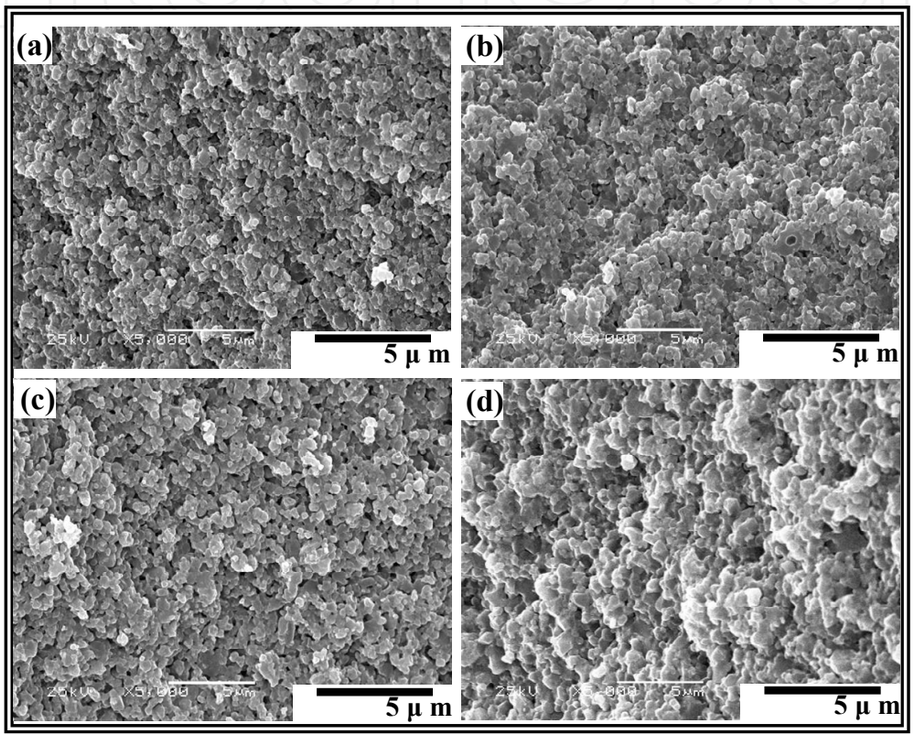


Fig. 7. Effect of sintering temperatures on Microstructure at 700 °C/min heating rate (a) 1300 °C, (b) 1400 °C, (c) 1450 °C, (d) 1500 °C.

Figure 7 (a) to (d) shows various SEM micrographs of fracture surfaces of the samples sintering at a high heating rate (700°C/min). The grain size is relatively small, less then 200 nm, compared to that in Fig. 6, but more porosities appear. We can conclude that, the heating rate of 200°C/min resulted in a homogeneous microstructure and an average grain size of about 500 nm. Essentially, the HFIHS process makes rapid sintering possible by application of a proper heating rate, and it also produces a sample with a low relative density and abnormal grains (as in samples made by a conventional method) when a lower heating rate is employed.

Experiments were conducted on synthesis and processing of nanostructured Alumina–20vol% 3YSZ composites sintered by HFIHS by S. W. Kim and Khalil (K. S. Won & Khalil, 2006). They conclude that, The Alumina micro-powder and 3YSZ nano-powders mixtures with distinct nanocrystalline characteristics were synthesized and optimized by using wet-

milling technique. This technique is remarkable due to the easiness of application. The samples were densified by heating to a sintering temperature in the range of 1100 to 1400 °C, and then rapidly cooled to 500 °C. The density of the samples kept increasing with the rising of the sintering temperature. A relative density more than 99% of theoretical density of the composites was achieved after sintering at 1370 °C. Al_2O_3-3YSZ composites with small grain size, homogeneous microstructure, higher density, hardness and toughness were successfully produced at relatively low temperatures.

Mg/HAp nanocomposites were successfully synthesized using a high-frequency induction heat sintering method by Khalil and A. Almajid (Khalil &A. Almajid, 2012). They conclude that, HFIHS was effective in preparing fine crystalline, nearly fully dense Mg/HAp nanocomposites from powders with smaller crystal sizes by optimizing the overall processing parameters. The relative densities and microhardness values of the specimens increased with increasing sintering temperature, reaching values as high as 99.7 % and 60 HV, respectively, at 550 °C. Meanwhile, at a sintering temperature of 580 °C, the microhardness and relative density slightly decreased. The crystal size of the sample sintered at 500 °C was approximately 37 nm. However, higher sintering temperature resulted in an increase in crystal size. The compressive strength of the sample sintered at 500 °C was low, approximately 192.7 MPa. However, as the sintering temperature of the nanocomposites increased, the compressive strength increased. For example, the compressive strength of the nanocomposite sintered at 550 °C reached as high as 194.5 MPa. For the sample sintered at 580 °C, however, the compressive strength decreased to approximately 62.5 MPa due to an increase in grain size, as observed by FE-SEM. By increasing the applied sintering pressure from 30 to 50 MPa, the relative density and microhardness of the samples greatly increased. When the applied pressure increased from 50 to 80 MPa, the effect was small. The results of crystal size measurements reveal an increase in crystal size with increasing sintering pressure of nano-size HAp reinforcements in the magnesium matrix. High applied pressure during sintering leads to an increase in the apparent activation energy and, subsequently, to an increase in crystal size. The ductility of the composite samples was found to be dependent on the increase in crystal size during sintering. The effect of sintering time on the mechanical and microstructural properties of composite samples has been reported. In this study, the relative density and microhardness increased with increasing sintering time up to 99.7% and 60 HV, respectively, after a 3-min holding time and then decreased with increasing sintering time. Sintering for a relatively short time produces small crystal sizes, but at the same time, the relative density is low. The compressive strength was significantly improved with increasing sintering time up to 3 min and then decreased when sintering for 4 min. The highest compressive strength of 192.7 MPa for sintered Mg/HAp samples was obtained at a sintering time of 3 min, whereas maximum compressive strengths of 154 and 137 MPa for the sintered samples were obtained at sintering times of 1 and 4 min, respectively. The density and microhardness increased with increasing heating rate, reaching a maximum level at a heating rate of 400°C/min. Meanwhile, at heating rates above 400°C/min, the relative density of the specimens decreased with an increase in the heating rate. The crystal size is strongly influenced by variation of the heating rate. High heating rates produce very fine crystal sizes, nearly 34 nm at 1200 °C/min. A heating rate of 400 °C/min produces small crystals (around 38.7 nm) with desirable mechanical properties. Samples sintered at a low heating

rate of 200 °C/min showed greater ductility and a low compressive strength of approximately 185 MPa. The compressive strength was slightly increased by increasing the heating rate up to 400 °C/min, reaching as high as 192.7 MPa, followed by a decrease with increasing heating rates.

M. Dewidar, (M. Dewidar, 2010) used high frequency induction heating sintering method for sintering high density compacts, containing as small grains as possible of powders. The alloy of Ti–6Al–4V was modified by addition of 2.5, 5, and 10 wt.% tungsten through powder metallurgy. The use of the high frequency induction heating sintering technique allows sintering to nearly full density at comparatively low temperatures and short holding times, and therefore suppressing grain growth. Different process parameters such as sintering temperature, and applied pressure have been investigated. The obtained compacts are characterized with respect to their densities, grain morphologies and pore distributions as well as hardness. Ti–6Al–4V/W powder precursors have been successfully compacted and consolidated to densities exceeding 98.8%. The maximum compressive strengths were obtained at sintering temperature 1000 °C for the samples containing 5% W, and at 1100 _C for the samples with 10% W. Maximum hardness was obtained 45 HRC at 1100 °C for 10% W.

4. Summary

Densification of nanocrystalline ceramic materials have been the subject of interests and focus of research programs around the world for the past two decades owing to the expectations that the mechanical behavior may improve significantly when grain sizes reduce to nanometer scale. Studies of nanopowder densification have lead to a better understanding of numerous sintering issues such as powder agglomeration, surface condition or contamination, pore role in sintering and grain growth. The resultant control of synthesis (e. g., non-agglomerated nanopowders) and processing has enabled fabrication of fully dense nanocrystalline parts particularly ceramic. However, although numerous technologies are available for making nanosized ceramic powders, obtaining true nanocrystalline ceramic (average grain size <100 nm) has been a great challenge due to the difficulties of controlling grain growth during sintering. Thus, the use of conventional methods of powder consolidation often result in grain growth in the compact or surface contamination due to the high temperatures and long sintering duration involved. It is therefore essential to minimize grain growth through careful control of the consolidation parameters, particularly sintering temperature and time. The challenges and results of sintering nanocrystalline ceramic powders have been summarized as well as the various technologies for producing nanosized ceramic powders. This chapter provides an overview of the development of nanocrystalline ceramic materials. Major improvements in the nanopowder synthesis methods and understanding of the densification process have resulted in fully dense parts by the largest multitude of sintering techniques, including conventional sintering.

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6. References

Allen, A.J., Kruegger, S., Skandan, G., Long, G.G., Hahn, H., Kerck, H.M., Parker, J.C., Ali, M.N., 1996. Microstructural evolution during the sintering of nanostructured ceramic oxides. J. Am. Ceram. Soc. 79, 1201–1212.

Agarwal DK, Cheng J, Fang Y, Roy R. Microwave processing of ceramics, composites and metallic materials. In: Clark DE, Folz DC, Folgar CE, Mahmoud MM, editors. Microwave solutions for ceramic engineers. Ohio: The American Ceramic Society; 2005. p. 205–28.

Aravindan S, Ramkumar J, Malhotra SK, Krishnamurthy R. Enhancement of cutting performance of cemented carbide cutting tools by microwave treatment. In: Clark DE, Folz DC, Folgar CE, Mahmoud MM, editors. Microwave solutions for ceramic engineers. Ohio: The American Ceramic Society; 2005. p. 255–62.

Breval E, Cheng JP, Agarwal DK, Gigl P, Dennis M, Roy R, et al. Comparison between microwave and conventional sintering of WC/Co composites. Mater Sci Eng A 2005;391:285–95.

Clark D, Sutton WH. Microwave processing of hard metals. Annu Rev Mater 1996;26:299–331.

Cheng J. Study on microwave sintering technique of ceramic materials. Ph. D. Thesis. Wuhan University of Technology, China; 1991.

Cheng JP, Agarwal DK, Komarneni S, Mathis M, Roy R. Microwave processing of WC–Co composites. Mater Res Innov 1997;1:44–52.

C.Y. Tang, P.S. Uskokovic, C.P. Tsui, Dj. Veljovic, R. Petrovic, Dj. Janackovic, Influence of microstructure and phase composition on the nanoindentation characterization of bioceramic materials based on hydroxyapatite, Ceram. Int. 35 (2009) 2171–2178.

C. Leonelli, P. Veronesi, L. Denti, A. Gatto, L. Iuliano, Journal of Materials Processing Technology 205 (2008) 489–496.

Committee on Microwave Processing of Materials: An Emerging Industrial Technology, National Materials Advisory Board, Commission on Engineering and Technical Systems, and National Research Council, "Microwave Processing of Materials," Pub. NMAB-473, National Academy Press, Washington D.C., 1994.

C. Elissalde, M. Maglione, C. Estournes, Tailoring Dielectric Properties of Multilayer Composites Using Spark Plasma Sintering.J. Am. Ceram. Soc. 90 (2007) 973–976.

D. Agrawal, Microwave Sintering of Ceramics, Composite, Metals, And Transparent Materials, Journal of Materials Education 19, Nrs. 4-6, 49–58, (1997)

D. Agrawal, Sohn MICROWAVE SINTERING, BRAZING AND MELTING OF METALLIC MATERIALS, International Symposium Advanced Processing of Metals and Materials, vol. 4, 2006, pp. 183–192.

D.E. Clark, D.C. Folz, J.K. West, Processing materials with microwave energy, Materials Science and Engineering A 287 (2000) 153–158.

Dj. Veljovic´, B. Jokic´, R. Petrovic´, E. Palcevskis, A. Dindune, I.N. Mihailescu, Dj. Janac´kovic´, Processing of dense nanostructured HAP ceramics by sintering and hot pressing, Ceram. Int. 35 (2009) 1407– 1413.

Dj. Veljovic, B. Jokic, I. Jankovic-Castvan, I. Smiciklas, R. Petrovic, Dj. Janackovic, Sintering behaviour of nanosized HAP powder, Key Eng. Mater. 330–332 (2007) 259–262.

Godlinski, D., Kuntz, M., Grathwohl, G., 2002. Transparente alumina with submicrometer grains by float packing and sintering. J. Am. Ceram. Soc. 85, 2449–2456.

Gerdes T & Porada MW, Microwave sintering of metal–ceramic and ceramic– ceramic composites. Mater Res Soc Symp Proc 1994;347:531–7.

H. Borodianska, L. Krushinskaya, G. Makarenko, Y. Sakka, I. Uvarova and O. Vasylkiv Si3N4–TiN Nanocomposite by Nitration of TiSi2 and Consolidation by Hot Pressing and Spark Plasma Sintering J. Nanosci. Nanotechnol. 9[11] (2009) 6381-6389 DOI:10.1166/jnn.2009.1344

H. Borodianska, O. Vasylkiv and Y. Sakka Nanoreactor Engineering and Spark Plasma Sintering of Gd20Ce80O1.90 Nanopowders J. Nanosci. Nanotechnol. 8[6] (2008) 3077-3084 DOI:10.1166/jnn.2008.087

Inoue (K.), US Patent, N° 3 241 956 (1966).

J.R. Groza, Nanosintering, Nanostruct. Mater. 12 (1999) 987–992.

J. Gurt Santanach, C. Estourn s, A. Weibel, A. Peigney, G. Chevallier and C. Laurent, Spark plasma sintering as a reactive sintering tool for the preparation of surface-tailored Fe-FeAl2O4-Al2O3 nanocomposites Scripta Materialia 60(4), (2009), 195-198.

J.K. Park, U.J. Chung, D.Y. Kim, Application of spark plasma sintering for growing dense Pb(Mg1/3Nb2/3)O3–35 mol% PbTiO3 single crystal by solid-state crystal growth, J. Electroceram. 17 (2006) 509–513.

J. Zhang, L. Wang, L. Shi, W. Jiang, L. Chen, Scripta Mater. 56 (2007) 241–244.

Jiang, D., Hulbert, D.M., Kuntz, J.D., Anselmi-Tamburini, U., Mukherjee, A.K., 2007. Spark plasma sintering: a high strain rate low temperature forming tool for ceramics. Mater. Sci. Eng. A 463, 89–93.

Kolaska H, Porada MW, Rodinger K, Gerdes T. Composite and process for the production thereof. 2000: US patent no. 6124040.

K. Kakegawa, N. Uekawa, Y.J. Wu, Y. Sasaki, Change in the compositional distribution in perovskite solid solutions during the sintering by SPS, Mater. Sci. Eng. B 99 (2003) 11-14.

K.A. Khor, X.J. Chen, S.H. Chan, L.G. Yu, Microstructure-property modifications in plasma sprayed 20 wt.% yttria stabilized zirconia electrolyte by spark plasma sintering (SPS) technique, Mater. Sci. Eng. A 366 (2004) 120-126.

Khalil Abdelrazek Khalil and Sug Won Kim, Effect of Processing Parameters on the Mechanical and Microstructural Behavior of Ultra-Fine Al2O3- (ZrO2+8%Mol Y2O3) Bioceramic, Densified By High Frequency Induction Heat Sintering, Int. Journal of Applied Ceramic Technology, 3 [4], 322–330 (2006)

Khalil Abdelrazek Khalil and Sug Won Kim, High-Frequency Induction Heating Sintering Of Hydroxyapatite-(Zro2+3%Mol Y2o3) Bioceramics, Materials Science Forum Vols. 534-536 (2007) pp. 601-604.

Khalil Abdelrazek Khalil and Sug Won Kim, Synthesis and Densification of Ultra-Fine Al2o3-(Zro2+3%Mol Y2o3) Bioceramics by High-Frequency Induction Heat Sintering, Materials Science Forum Vols. 534-536 (2007) pp. 1033-1036.

Khalil Abdelrazek Khalil, Sug Won Kim, and Hak Yong Kim, Observation of Toughness Improvements of the Hydroxyapatite Bioceramics Densified by High-Frequency

Induction Heat Sintering, Int. Journal of Applied Ceramic Technology, 4 [1] 30–37 (2007)

Khalil Abdelrazek Khalil, Sug Won Kim, N. Dharmaraj, Kwan Woo Kim and Hak Yong Kim, Novel Mechanism to Improve Toughness of the Hydroxyapatite Bioceramics Using High-Frequency Induction Heat Sintering, Journal of Materials Processing Technology 187-188 (2007) 417–420

Khalil Abdelrazek Khalil and Sug Won Kim, Mechanical Wet-Milling and Subsequent consolidation of Ultra-Fine Al_2O_3-(ZrO_2+3%Mol Y_2O_3) Bioceramics by using High-Frequency Induction Heat Sintering, Trans. Nonferrous Met. Soc. China, 17(2007) 21-26.

Khalil Abdelrazek Khalil, Sug Won Kim and Hak Yong Kim, Consolidation and mechanical properties of nanostructured hydroxyapatite–(ZrO2 + 3 mol% Y2O3) bioceramics by high-frequency induction heat sintering, Materials Science and Engineering A 456 (2007) 368–372.

Khalil Abdelrazek Khalil & Abdulhakim A. Almajid, Effect of high-frequency induction heat sintering conditions on the microstructure and mechanical properties of nanostructured magnesium/hydroxyapatite nanocomposites, Materials and Design, in press, (2012)

Kim, S.W., Khalil, K.A.R., 2006. High-frequency induction heat sintering of mechanically alloyed alumina–yttria-stabilized zirconia nano-bioceramics. J. Am. Ceram. Soc. 89, 1280–1285.

Krell, A., Blank, P., Ma, H., Hutzler, T., van Bruggen, M.P.B., Apetz, R., 2003. Transparent sintered corundum with high hardness and strength. J. Am. Ceram. Soc. 86, 12–18.

Katz JD. Microwave sintering of ceramics. Annu Rev Mater Sci 1992;22:153–70.

M.J. Mayo, Nanocrystalline ceramics for structural applications: processing and properties, in: G.M. Chow, N.I. Noskova, Nanostructured (Eds.), Materials Science Technology, NATO ASI Series, Kluwer Academic Publishers, Russia, 1997, pp. 361–385.

Montasser Dewidar, Microstructure and mechanical properties of biocompatible high density Ti–6Al–4V/W produced by high frequency induction heating sintering, Materials and Design 31 (2010) 3964–3970

K. Morita, B.N. Kim, K. Hiraga, H. Yoshida, Fabrication of transparent MgAl2O4 spinel polycrystal by spark plasma sintering processing Scripta Mater. 58 (2008) 1114–1117.

Lin, F.J.T., de Jonghe, L.C., Rahaman, M.N., 1997. Microstructure refinement of sintered alumina by a two-step sintering technique. J. Am. Ceram. Soc. 80, 2269–2277.

Mishra, R. S., Risbud, S. H. & Mukherjee, A. K. Influence of initial crystal structure and electrical pulsing on densification of nanocrystalline alumina powder. Journal of Materials Research 13, 86-89 (1998).

Murayama, N. What can we do by pulsed electric current sintering? Seramikkusu 32, 445-449 (1997).

Mishra, R. S. & Mukherjee, A. K. Electric pulse assisted rapid consolidation of ultrafine grained alumina matrix composites. Materials Science & Engineering, A: Structural Materials: Properties, Microstructure and Processing A287, 178-182 (2000).

M. Omori, Sintering, consolidation, reaction and crystal growth by the spark plasma system (SPS), Mater. Sci. Eng. A 287 (2) (2000) 183–188.

O. VASYLKIV : "Nanoreactor engineering and SPS densification of multimetal oxide ceramic nanopowders" J. European Ceram. Soc. 28[5] (2008) 919-927

O. Vasylkiv, H. Borodianska, P. Badica, Y. Zhen and A. Tok : "Nanoblast Synthesis and Consolidation of $(La_{0.8}Sr_{0.2})(Ga_{0.9}Mg_{0.1})O_{3-\delta}$ Under Spark Plasma Sintering Conditions" J. Nanosci. Nanotechnol. 9[1] (2009) 141-149

P. Yadoji, R. Peelamedu, D. Agrawal, R. Roy, Microwave sintering of Ni-Zn ferrites: comparison with conventional sintering Materials Science and Engineering B 98 (2003) 269–278.

P. Angerer, L.G. Yu, K.A. Khor, G. Krumpel, Spark-plasma-sintering (SPS) of nanostructured and submicron titanium oxide powders Mater. Sci. Eng. A 381 (2004) 16.

R. Licheri, R. Orrù, C. Musa and G. Cao, "Combination of SHS and SPS Techniques for the Fabrication of Fully Dense ZrB_2-ZrC-SiC UHTC Composites", Materials Letters, 62, 432-435 (2008).

R. Chaim, R. Marder-Jaeckel, and J. Z. Shen, "Transparent YAG ceramics by surface softening of nanoparticles in spark plasma sintering", *Mater. Sci. Eng. A* 429, 74-78 (2006).

R. Chaim, M. Kalina, and J. Z. Shen, "Transparent Yttrium Aluminum Garnet (YAG) Ceramics by Spark Plasma Sintering", J. Eur. Ceram. Soc. 27, 3331-3337 (2007).

R.R. Menezes, P.M. Souto, R.H.G.A. Kiminami, Microwave hybrid fast sintering of porcelain bodies, J. Mater. Proc. Technol. 190 (2007) 223–229.

Rodinger K, Dreyer K, Gerdes T, Porada MW. Microwave sintering of hardmetals. Int J Refract Metals Hard Mater 1998; 16:409–16.

Ramkumar J, Aravindan S, Malhotra SK, Krishnamurthy R. Enhancing the metallurgical properties of WC insert (K-20) cutting tool through microwave treatment. Mater Lett 2002;53:200–4.

R. Halouani, D. Bernache-Assollant, E. Champion, A. Ababou, Microstructure and related mechanical properties of hot pressed hydroxyapatite ceramics, J. Mater. Sci: Mater. Med. 5 (1994) 563–568.

S. Vijayan, H. Varma, Microwave sintering of nanosized hydroxyapatite powder compacts, Mater. Lett. 56 (2002) 827–831.

Sug Won Kim and Khalil Abdelrazek Khalil, High frequency induction heating sintering of mechanically alloyed alumina-yttria stabilized zirconia nano-bioceramics, Journal of American Ceramic Society, Vol. 89, No. 4, p. 1280–1285 (2006).

W. Liu, M. Naka, In-situ joining of dissimilar nanocrystalline materials by spark plasma sintering. Scripta Materialia 48 (2003) 1225-1230.

Y.J. Wu, N. Uekawa, K. Kakegawa, Sandwiched $BaNd_2Ti_4O_{12}/Bi_4Ti_3O_{12}/BaNd_2Ti_4O_{12}$ ceramics prepared by spark plasma sintering Mater. Lett. 57 (2003) 4088–4092.

Y.W. Gua, K.A. Khora, P. Cheang, Bone-like apatite layer formation on hydroxyapatite prepared by spark plasma sintering (SPS), Biomaterials 25 (2004) 4127–4134.

Yoshimura, M., Ohji, T., Sando, M. & Nihara, K. Rapid rate sintering of nano-grained ZrO_2-based composites using pulse electric current sintering method. Journal of Materials Science Letters 17, 1389-1391 (1998).

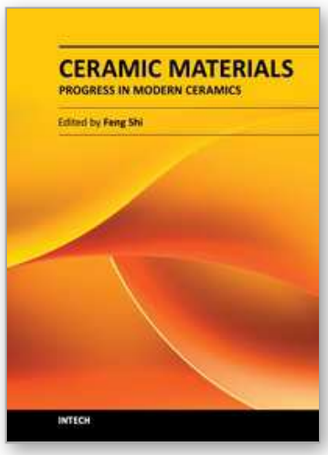
Z.A. Munir, U. Anselmi-Tamburini, M. Ohyanagi, J. Mater. Sci. 41 (2006) 763–777.

W.W. Wu, G.J. Zhang, Y.M. Kan, P.L. Wang, K. Vanmeensel, J. Vleugels, O. Van der Biest, Scripta Mater. 57 (2007) 317–320.

Zhou, Y., Hirao, K., Toriyama, M. & Tanaka, H. Very rapid densification of nanometer silicon carbide powder by pulse electric current sintering. Journal of the American Ceramic Society 83, 654-656 (2000)

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