

DEVELOPMENT OF CERAMIC COMPOSITES FOR IMPROVED TOUGHNESS

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CANDIDATE'S DECLARATION

I hereby declare that the proposed work presented in this dissertation entitled “**Development of Ceramic Composites for Improved Toughness** ” is in partial fulfillment of the requirements for the award of the degree of **Master of Technology** in **Materials Engineering**, submitted in the **Department of Metallurgical and Materials Engineering, Indian Institute of Technology Roorkee** is an authentic record of my own work carried out during the period of July 2015 to May 2016 under the supervision of **Dr. Anjan Sil, Professor and Head**, Department of Metallurgical and Materials Engineering, Indian Institute of Technology Roorkee, India. The matter presented in this dissertation has not been submitted by me for the award of any other degree.

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ABSTRACT

Ceramic based composites were reviewed, using the recently developed methods to improve the fracture toughness. Silicon carbide material was chosen because of its application in aerospace, automobiles and bulletproof vests. By conventional sintering abnormal grain growth occurs which reduces hardness, fracture toughness, Corrosion and wear resistance. To get fine grained structure, Silicon carbide composite with different content of cerium dioxide was prepared by spark plasma sintering at 1850 °C and 60 MPA. For high densification sintering additive was used. Effects of addition of nano sized cerium dioxide particles on microstructure and mechanical properties were studied. Around 12.9 % of improvement in hardness was measured, maximum at 0.1 wt. % of cerium dioxide and at 0.5 wt. % of cerium dioxide around 25 % of improvement in fracture toughness was measured.

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CHAPTER 1

INTRODUCTION

In our daily life role of ceramics is progressively increasing. People have started making daily use things from ceramics due to their unique properties. Ceramic materials are Inorganic and nonmetallic which are necessary for daily lifestyle. Things which we see around us most of them are ceramics like tile, bricks, plates, glass, and toilets [1]. Nowadays ceramics are used as tuning forks in watches, piezoelectric-ceramics in snow skis, as sparkplugs and ceramic engine parts in automobiles. Some phone lines and electric equipment are prepared by ceramics. Ceramics are also used in space shuttles and in airplanes (nose cones). Ceramics can be characterized as:

1.1 Traditional ceramics:

Those ceramics which have anionic system are known as traditional ceramics. These are also known as silicate ceramics. Traditional ceramics are prepared from cement and clay. They get hardness when they undergo very high temperature. Silicate ceramics are used to prepare bowls, bricks, pots for plants etc. to prepare traditional ceramics there is no requirement of any advanced processing the only thing which is required is high temperature.

1.2 Advanced ceramics:

These ceramics cannot be prepared by giving only high temperature but an advanced processing technique is also required. All carbides, nitrides, oxides, borides come in the category of advanced ceramics. These ceramics have wide range of applications where high hardness or high temperature sustainability is required [2].

On the basis of composition also ceramics can be differentiated as Oxide ceramics: Al_2O_3 , Cerium (IV) oxide, ZrO_2 etc. and Non oxide ceramics: This group contains carbon, nitrogen, boron group etc.

As science and technology is growing with rapid speed. For different type of applications different materials are required. Applications like multi-storey buildings, railway bridges, impact loading applications etc. high hardness and high toughness is required. As hardness was only the criterion then metallurgist develop ceramics but they loss ductility and toughness. Ceramics are brittle in nature and have very low toughness. Being a metallurgist our aim is to increase strength without reducing ductility and toughness. But toughness of ceramics has already been decreased so now metallurgists are trying to increase the toughness of ceramic composites without decreasing their strength. The main reason for low fracture toughness of ceramic is their bonding.

1.3 Bonding in ceramics:

Bonding in ceramic atoms is mainly ionic but some ceramics have covalent bonding in between their atoms. About the bonding in ceramic it can be said that atoms of ceramics have neither entirely covalent bonding nor totally ionic but the bonding of ceramic atoms have mixed character [2].

1.4 Toughness of ceramics:

Ionic and covalent bonds have very less vibrations and ions are closely bound due to this these bonds do not permit the dislocation motion. As dislocation motion is restricted in ceramics due to this ceramic have brittle character and shows very low fracture toughness. Many efforts were made to increase the fracture toughness of ceramics. Many additives were added during the sintering, liquid phase sintering was done and appropriate results were obtained. Some materials like silicon carbide, Silicon nitride, tungsten carbide, aluminium oxide, zirconia, zirconium boride, aluminium nitride etc. on which scientists made attempts to improve fracture toughness and reduce the sintering temperature.

From last two decades' scientists are concentrating to improve fracture toughness of ceramics. Nowadays ceramics have applications in aerospace industries, in automobile industries, also in bullet proof vests. If the fracture toughness and strength of ceramics can be improved then lot of material can be saved and the weight automobiles, air shuttles and bulletproof vests will be reduced.

Table 1.1 Properties of some widely used ceramics.

Material	Melting point °C	Density g/cm ³	Elastic modulus GPa	Strength MPa	Fracture Toughness MPa.m ^{1/2}	Coefficient of thermal expansion x10 ⁻⁶ /°C
Al ₂ O ₃	2050	4.0	380	455	3.5	8.0
AlN	1900	3.3	320	441	2.6	4.4
B ₄ C	2350	2.5	450	350	3.3	4.3
SiC	2700	3.2	210	140	3-5	4.3
WC	2870	15.8	700	600	8.5	5.2
ZrO ₂	2960	5.6	140	175	13	7.5

1.5 History of ceramics

According to Archaeologists first time ceramics were prepared by human during 26,000 B.C. That time human and animal statues, spheres and blocks were prepared. To prepare these very thin catlinite material, animal bone, ash of bones and animal fat were heated at temp. 500-800 °C in closed rounded vault after the forming process. Uses of the spheres and blocks are not clear till now. It is assumed that the blocks would be used to make structures and statues were used for decoration purpose. Archaeologists found first use of ceramics was during 9,000 B.C. In this time period pottery vessels were prepared from china clay. These vessels were used to carry and reserve seeds and fruits.

A great revolution came in the field of ceramic during 4,000 B.C. when a large no. of pottery was prepared from china clay and glass was also prepared during this period in primitive Egypt that ancient glass had coating of silicate upon quartz. This was start of ceramic coating which is continuous till present time. Ceramic coating is used on multiple items like bathtubs, kitchen utensils etc. In the period of 50 B.C.-50 A.D. reflecting glasses and lenses were prepared in the same period of time glass of windows were also produced in Rome. After that Chinese people develop ceramic composite during 600 A.D. named Porcelain which was the product of feldspar, earth and quartz. In 1870's production of refractory materials begins which were able to sustain very high temperatures. To disclose the secret of advanced ceramics The American Ceramic Society was inaugurated in 1889. Officially first brick and tiles factory opened in 1894 in the western part of Romania. After that in 1960 optical fibers were invented just after the invention of laser. After five years in 1965 to use solar energy Photo Voltaic cells were discovered. In 1987 superconducting oxides of ceramic having 92 K as critical temperature were invented which is used in IC's of high speed computers. In 1992 some ceramics named as smart materials [3] which can react with atmosphere of surface were invented. People strongly believe that ceramics played a very important role in advancement of mankind. From that time the technology and uses of ceramics are regularly increasing and a continuous progress in the field of ceramics is going on.

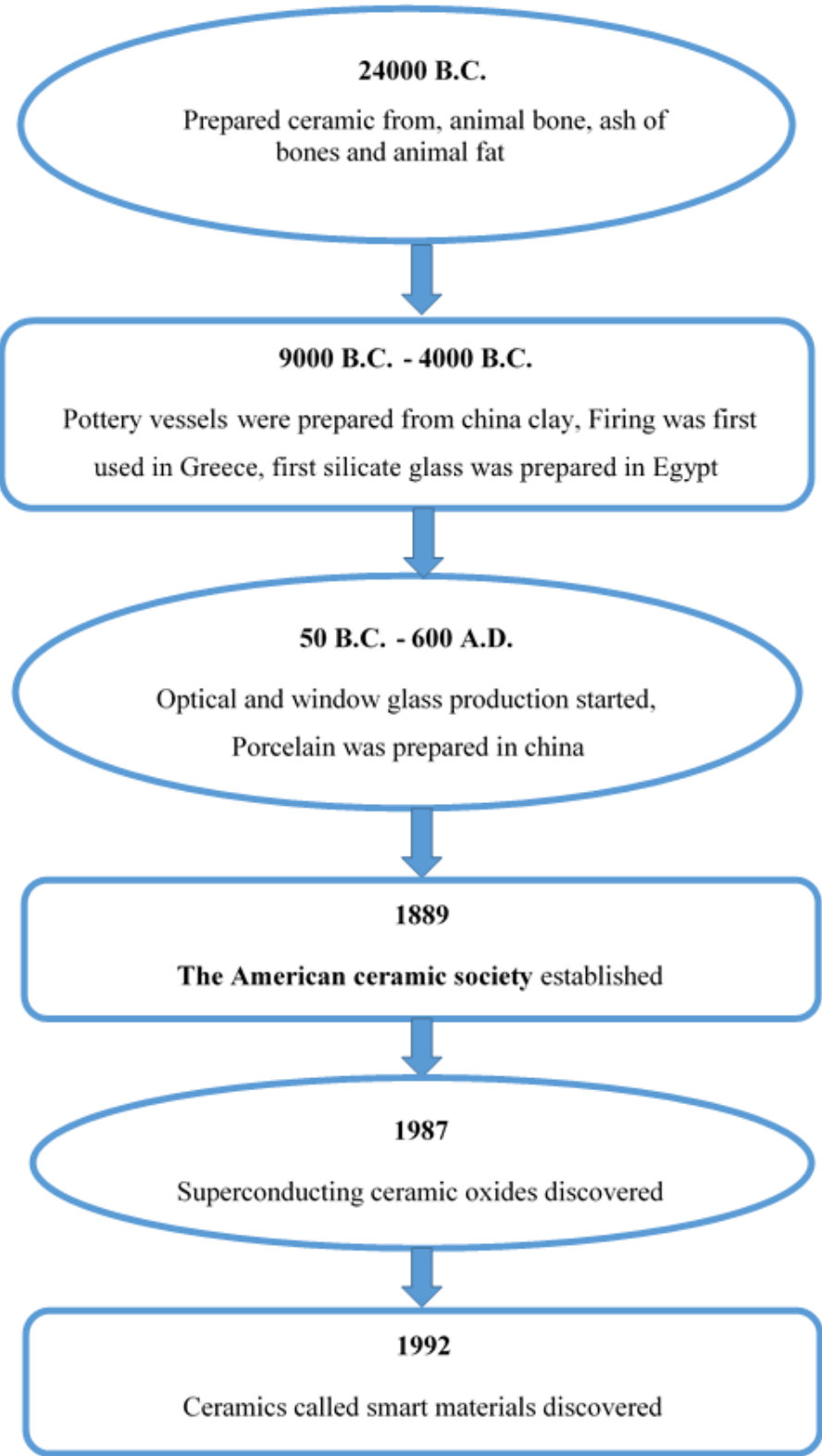


Figure 1.1 Flowchart shows history of ceramics.

1.6 Silicon Carbide:

As from above table it can be seen that silicon carbide has high melting point though sintering of silicon carbide is difficult. To sinter silicon carbide high temperature is required or sintering additive required. The property of silicon carbide which attracts the researchers is density. Silicon carbide have very low density i.e. 3.21 g/cm^3 and shows good oxidation resistance, good thermal shock, wear and chemical resistance, and good strength at high temperature [4]. Because of these properties silicon carbide has wide range of applications.

1.7 Applications of silicon carbide are:

1.7.1 As Abrasive:

It is widely used as abrasive because of its hardness and low cost. It is used on grinders, emery papers and as abrasive material in water jet cutting and wear testing.

1.7.2 As cutting tool:

After the innovation of SiC- Al_2O_3 whiskers 1st cutting tool of this whisker came in market in 1985. Nowadays cutting disks (figure 1.2) are prepared from silicon carbide [5].



Figure 1.2 Silicon carbide cutting disk.

1.7.3 As constructional material:

Silicon carbide have many applications in defense [6]. Many components like bulletproof vests (figure 1.3), chobham armour which is used to protect main battle tanks [7] and dragon skin (figure 2 b) are prepared by using silicon carbide.



Figure 1.3 (a) Bulletproof vest, (b) Dragon skin.

Silicon carbide have many applications in aerospace. Due to its high temperature wear and shock resistivity. Airplane nose (figure 1.4) is prepared by silicon carbide.



Figure 1.4 Airplane Nose.

Silicon carbide is widely used in automobiles. Automobile parts like brakes and clutches plates (figure 1.4) and diesel filters.



Figure 1.5 Clutch plate made of silicon carbide.

1.7.4 In Electronics:

Silicon carbide also have its applications in electronic elements. Silicon carbide based Chips, power MOSFET's [8], CIPS [9] and bipolar transistors are prepared by using silicon carbide. 1st blue LED was also prepared by silicon carbide during 1980's.

1.7.5 In Nuclear Reactor:

Coating of nuclear fuel particles is of silicon carbide. A layer of silicon carbide gives structural support to coated fuel particles which protect fuel particles from deformation. Researches are thinking to use Silicon carbide composite as a replacement of Zirconium alloy cladding in light water reactors.

CHAPTER 2

LITERATURE REVIEW

This literature review deals with the methods used for the sintering, steps taken to decrease sintering temperature and steps taken to improve fracture toughness of ceramics and densification rate at low temperature.

2.1 Development of ceramics:

Sintering method is used to develop ceramics. During the sintering process diffusion of atom takes place across the particles border. During sintering compaction of powder takes place by the use of pressure or high temperature or by using pressure and temperature both and a solid mass formation takes place [10]. Sintering decreases, the porosity of powder and upgrades the properties like fracture toughness, strength etc. and reduces the thermal and electrical resistivity [11]. During sintering process surface area reduces due to this reduction in surface free energy takes place. This reduction in free energy works as the activation power for the diffusion of atoms [12]. The salient thing which is required to manage is temperature because it supervise the diffusion and controls the grain growth. Two types of sintering are done one is pressure less sintering [13] other is sintering using pressure [14]. Pressure less sintering is only applicable for classified metal ceramic composite. For pressure less sintering pre-compacted sample is required named as green compacts or samples [15]. These are highly porous. Green compacts generally show density around 70 %. This 30 % of porosity of green compacts can be reduced by further compression at high pressure using cold isostatic press. But further compression does not enhance density too much only 4-5 % of density change takes place. In conventional sintering process density of pure materials does not goes above 85-90 %. To increase the density some additives (metals, less melting point materials) are to be used [16]. During pressure less sintering metal melts and enhance the diffusion rate [17]. To achieve high density then pressure is used during sintering. Better compaction takes place in pressure sintering [18]. Both the processes consume lot of time. It is difficult task to maintain the high pressure for a long time for the material like SiC, B₄C and BN etc.

Nowadays advanced technology (spark plasma sintering) is used to sinter the ceramics [19]. It is very effective because of its quickness and compaction. When normal pressure sintering takes 8 to 10 hours, SPS takes only 5 to 10 minutes and gives better properties [20] and around 100 % of density can be obtained [21]. But for SPS also it is difficult to get ~100 % density in case of pure ceramic materials small amount of additives are used. For pure silicon carbide maximum density observed by spark plasma sintering is not 97.5 % [22] but this density was observed at high pressure. For the normal pressure maximum density of pure SiC is observed around 90 % [23].

2.2 Fracture Toughness:

Fracture toughness is the ability of material which resist crack propagation. Unit of fracture toughness is $\text{MPa m}^{1/2}$ [24]. By stress intensity factor denoted by K fracture toughness can be measured. The simplest method to measure fracture toughness is indentation method. Due to indentation crack generation takes place and by using that crack length fracture toughness can be calculated.

2.3 Improvement in Toughness:

The requirement of obtaining both high fracture toughness and high densification rate at low sintering temperature are in focus from last few decades and from all the distinct approaches, reducing particle size [25], reducing grain size [26], introduction of second phase by liquid phase sintering [27] and solid state sintering [28] with sintering additives [29], has been greatly examined. Present research work on ceramics is predominantly focused on the techniques to improve fracture toughness of ceramics.

Choi et al. [30] have reported that by reducing the particle size fracture toughness of material increases. Nano sized aluminium oxide was taken and 5-wt. % nickel and three volume % Silicon carbide were the sintering additives after ball milling sintering was done at 1400 °C. Then fracture toughness, relative density, creep resistance, wear resistance and flexural strength were improved. Due to difference in coefficient of thermal expansion crack generation takes place but if particle size is very small then size of crack will be very small which will be comparable to dislocation or it may possible that in place of crack generation dislocation will generate. These dislocations will be at the surface of particle. After that annealing can be done to enhance the properties.

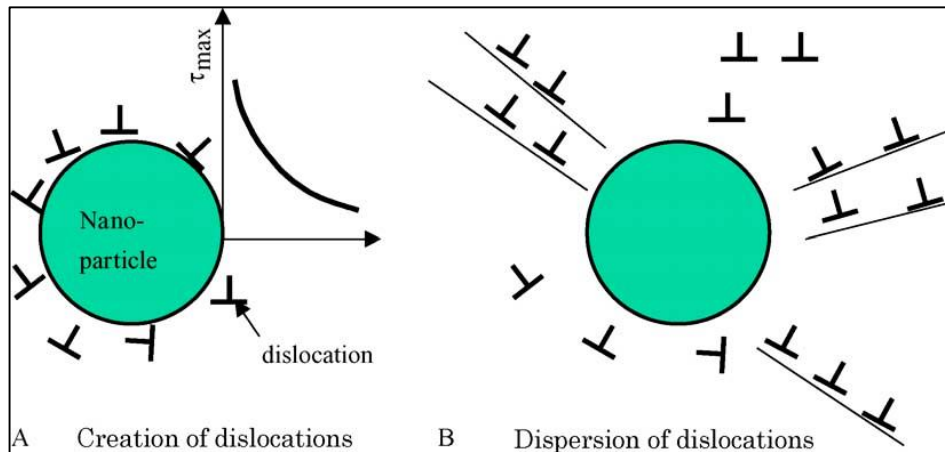


Figure 2.1 (a) Dislocations after sintering and, (b) after annealing.

Due to annealing dispersion of dislocations in matrix takes place and secondary grain boundary formation takes place. When crack comes near these sub grain boundary dislocations converts in to small Nano sized cracks. Due to formation of nano cracks stress at the crack tip will be resolved. Due to this fracture process zone's strength will improve and fracture toughness will improve.

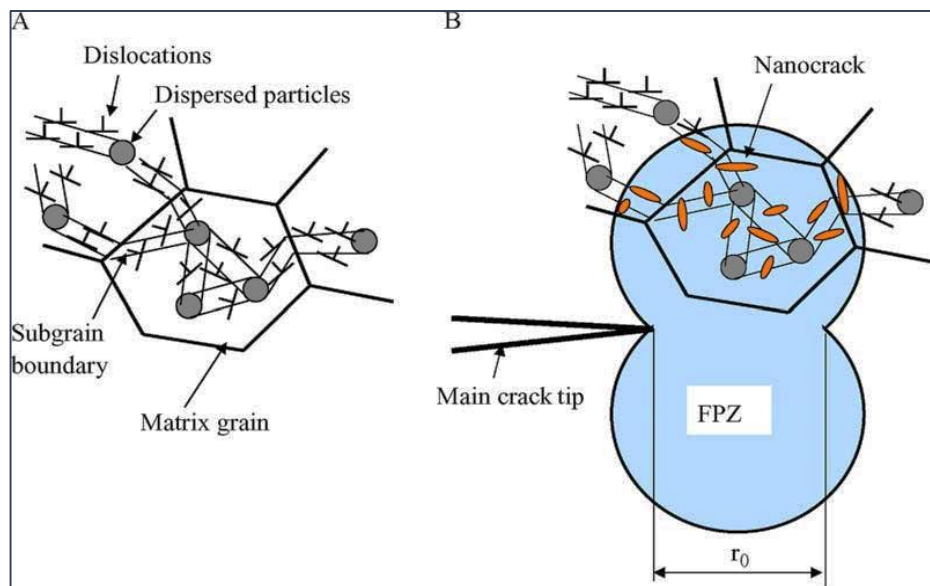


Figure 2.2 Toughening mechanism in Nano composites (a) Intra-type Nano-structure after annealing, (b) Fracture process zone strengthening.

Boussois et al. [31] in the year 2014 reported the high toughness of silicate ceramics after the addition of alumina fibers and kaolin. Porcelain was taken and fibers were used as build-up phases. It was seen that crack propagation was directly related to microstructural properties. Heat treatment was used to arise mullite phase at 1100 °C. In mullite crystals are highly connected and favors dislocation motion. Due to this improvement in strength and fracture toughness was observed and thermal conductivity and thermal coefficient of expansion were decreased, creep resistance and high temperature resistance were enhanced. Fracture toughness was improved from 1.8 MPa m^{1/2} to 4.6 MPa m^{1/2}. Zirconium oxide experiences phase change at temperature 1000 °C and 2370 °C during this volume changes and due to this it has high toughness. Zirconium oxide have applications in high temp. sensors.

Hirvonen et al. [32] reported that fracture toughness and strength of zirconia established Nano composite can be improved by addition of cordierite (2MgO.2Al₂O₃.5SiO₂). Zirconia stabilized by yttrium and cordierite powders were mixed by using ball milling. Then uniaxial pressing at 29.4 MPa was done on the powder to prepare rectangular sample. Then to increase the green density of sample cold isostatic press was used. Highest green density was obtained at 196 MPa. Then pressure less sintering was done at 1400 °C. A small amount of increment in fracture toughness and strength was observed at 5 volume % of cordierite.

Silicon carbide attracts researchers due to its good properties like low density strength, low thermal resistivity, corrosion resistance and hardness. It has wide range of applications due to its high resistance to corrosion it is used to prepare tiles, bricks. Due to high temperature sustainability it is used as thermal blockage in aerospace. Due to its high hardness and less mass per unit volume it is used as bulletproof vests and armor. The main problem with silicon carbide is that sintering is difficult and its low fracture toughness. Past studies shows that by using additives sintering temperature can be lowered. Many additions like aluminium oxide and yttrium aluminium garnet (YAG) were checked as sintering additives for SiC [33]. After the addition of these two rate of densification was increased due to liquid phase sintering and grain growth decreased. Mechanism for both the additives was studied differently. As aluminium oxide is used then alumina and carbon supports the sintering by solid state sintering around 2000 °C. But when both aluminium oxide and yttria

are used then liquid phase sintering took place below 2000 °C and densification was increased.

Niihara et al. [34] reported that Second phase formation takes place when additives are used for sintering. The second phase forms at the grain boundary. Due to second phase crack deflection takes place. Si₃N₄ and SiC powders were used to make ceramic Nano composite. At 25 volume % of silicon carbide maximum fracture toughness was measured that was 10 % more than single phase Silicon nitride. Corrosion resistance of the second phase was less when liquid sintering was done or when additive was soft then matrix. To overcome this problem boron and carbon were added as additives then it was observed that hot pressing response was increased due to presence of boron carbide [35].

Maiti et al. [36] reported that soaking time effects the fracture toughness of ceramic composites. Sintering of alumina was done at different temperatures with different soaking time by conventional sintering method and it was found that fracture toughness of the sample which was sintered at 1700 °C has low fracture toughness then the samples which were sintered at 1500 and 1600 °C. It was because at 1700 °C larger grains were formed and trans granular fracture mode was predominant.

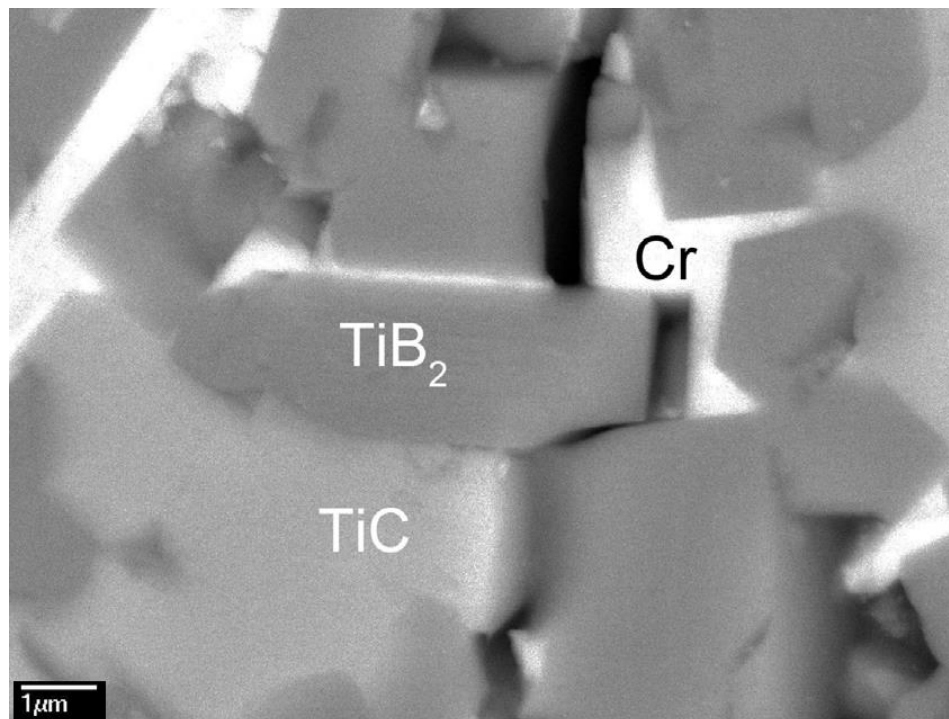


Figure 2.3 Crack deflection by second phase [37].

Boron Carbide is 3rd known hardest material [38]. Due to its high hardness it is used in cutting tools and bullet proof vests. It also has applications as substrate due to its low thermal resistivity and expansion. *Yue et al.* [39] reported great improvement in fracture toughness and strength and a little decrement in hardness after the addition of TiB₂ in B₄C. Mixture was prepared by stirring at 85 °C. Composition of mixture was varied from 19 to 45 mass % of TiB₂. Rectangular samples were prepared by uniaxial press and then sintered at 1950 °C. Three-point bending test was used to measure strength and indentation technique was used to measure the fracture toughness and hardness. Highest mechanical properties were measured at 43 mass % TiB₂. Fracture toughness and strength was increased by 1.5 MPa m^{1/2} and 153 MPa respectively. Because due to increase in amount of TiB₂ grain size reduced. Other reason for the increment in fracture toughness was the difference in coefficient of thermal expansion. Corrosion resistance was decreased with the increase in the content of TiB₂ because of less chemical stability and higher conductivity of TiB₂ than B₄C. Hardness was also decreased because of the low hardness of TiB₂.

Tungsten carbide (WC) have high hardness and used in cutting tools. Small amount of cobalt addition enhances its properties. It was found that cobalt is right match for tungsten carbide. 4-17 wt. % of cobalt with tungsten carbide studied [40]. It was found that WC-12Co is giving better properties than other proportions. It was found that fracture toughness was increased and sintering temperature was reduced.

Sun et al. [41] reported that hardness, strength, fracture toughness and wear resistance of Nano sized grained composite of WC-12Co is higher than the coarse grained structure.

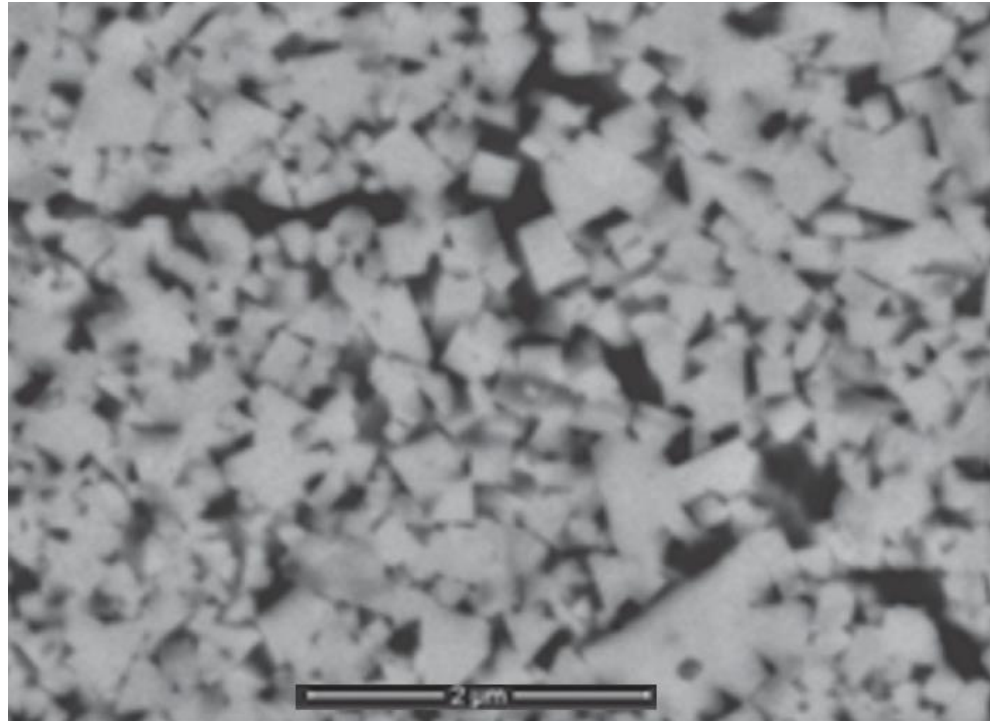


Figure 2.4 Crack deflection by grain boundary [41].

Tungsten carbide and cobalt powder were starting materials. Amount of ceria powder was varied from 0 to 0.6 wt. % in the composite. Powders were mixed by using ball mill. Sintering was done by using Spark plasma sintering at temperature 1200 °C and 50 MPa. Fracture toughness and hardness were measured by indentation method. Maximum relative density was measured at 0.5 wt. % of ceria. After that density decreased because ceria particles in liquid cobalt reduces the flow ability. Wear rate was minimum at 0.1 wt. % of ceria and Fracture toughness was increased by 13.4 % at 0.1 wt. % of ceria. Ceria restricted the irregular grain growth, 35 % decrement in grain size took place till 0.1 wt. % of ceria powder. More addition of ceria powder does not show any effect in grain size. After 0.1 wt. % of ceria cobalt pool formation started which reduces the relative density, fracture toughness and strength.

2.4 Problem Formulation:

Ceramics have very low fracture toughness due to this limitation ceramic have limited application as structural material. Also it is very difficult to sinter ceramics and get ~100 % density at low sintering temperature. The aim of this work is to get fully dense silicon carbide composite by spark plasma sintering at low sintering temperature and to increase fracture toughness of composite without losing its hardness. From literature it was found that fracture toughness of ceramics can be increased by reducing grain size and introducing second phase. To improve fracture toughness of silicon carbide, alumina and cerium dioxide are to be used as sintering additive. No one has reported any work on this composite.

CHAPTER 3

PLAN OF WORK

Whole work is mainly focused on the improvement of toughness of ceramic composite. For this purpose, we have chosen silicon carbide material as matrix and alumina and cerium dioxide as ceramic additives. The main function of alumina is to increase the densification rate of silicon carbide and also it will work as second phase. Cerium dioxide is added to restrict grain growth.

Fracture toughness of ceramics depend on particle size, grain size, and phases present. FESEM and XRD images were taken after and before ball mixing to measure the particle size, powder particles distribution and phase distribution.

To increase the density and mechanical properties advanced method of sintering (spark plasma sintering) was performed and circular samples with 10 mm diameter and 3 mm height were prepared. Density was calculated by Archimedes' principle.

Fracture toughness and hardness were calculated. To calculate fracture toughness and hardness indentation method was used. To determine the fracture toughness scanning electron microscopy was performed on indent to measure crack length. By using that crack length fracture toughness was measured.

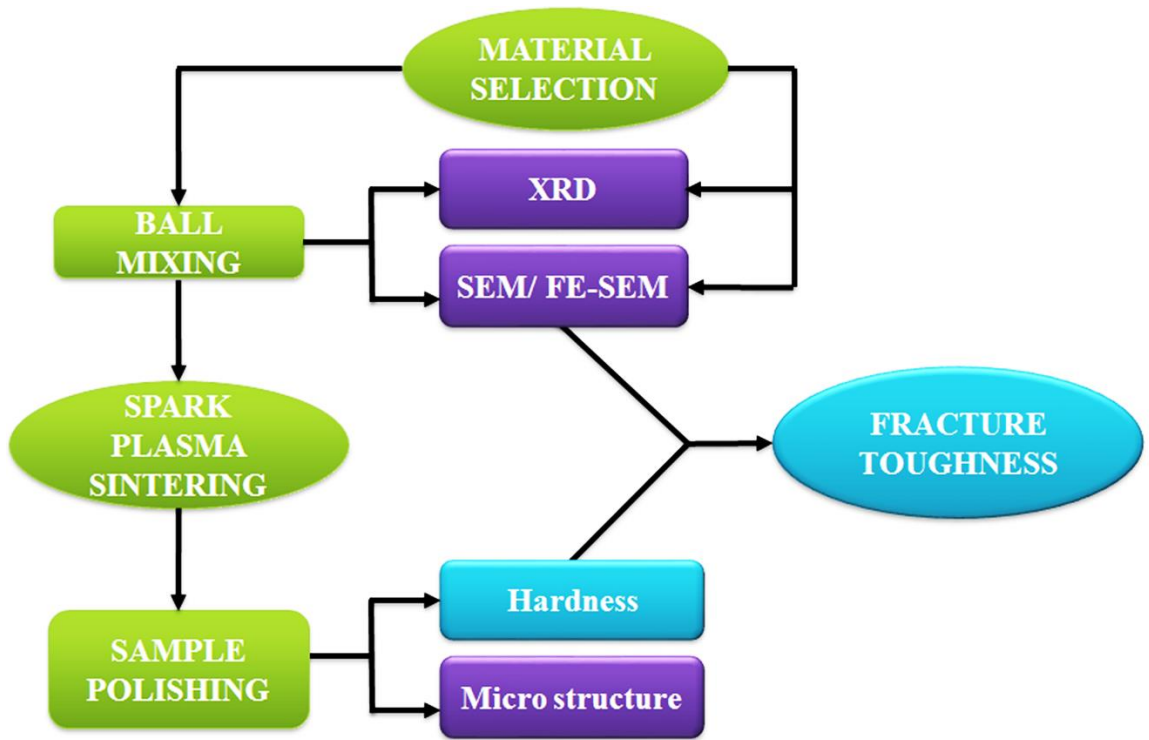


Figure 3.1 Flowchart showing plan of work.

CHAPTER 4

EXPERIMENTAL PROCEDURE

For the work ultra-fine Silicon carbide powder (SiC-99 % purity) is selected as the base material, and very small amount of cerium di-oxide and alumina is used as reinforcement.

4.1 Scanning Electron Microscopy (SEM)

Scanning electron microscope is that type of microscope in which formation of image is not done by the light but by the help of electron. In place of lenses electromagnets are used in scanning electron microscopy. Due to its high depth of field scanning electron microscopy gives many advantages as compared to conventional microscope. After the discovery of SEM i.e. 1950 it is giving chance to researchers to observe very closely spaced specimens at higher resolution.

As magnified image is produced by electrons which are produced by electron gun. Produced electron beam travels vertically downwards which passes through microscope, lenses and electromagnetic fields where vacuum is maintained.

To see the nano sized particles a high resolution microscopy such as field emission scanning electron microscopy (FE-SEM) is required in which High energy electrons are used to see the object at a very fine level. In standard scanning electron microscopes, electrons are generated from a tungsten filament (electron gun) when it is heated. But in a field emission (FE) scanning electron microscope, electron beam does not produce by heating filament, whereas Electrons are emitted from the surface of a conductor due to a strong electric field. Electric field is generated by voltage acceleration of magnitude of 0.5 to 30 kV between cathode and anode.

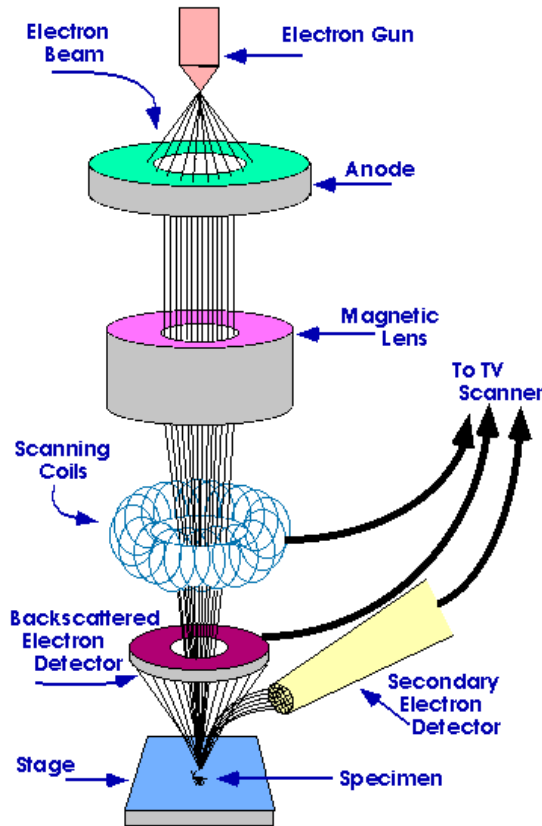


Figure 4.1 Schematic diagram of Scanning Electron Microscope.

The electrons which are produced by electron gun are known as primary electrons. When the primary electron beam strikes the conductive sample (sample must be conductive to perform scanning electron microscopy if sample is nonconductive then coating of sample is done by a conductive material which may be gold coating or platinum coating) then secondary electron as well as X-rays emits from sample.

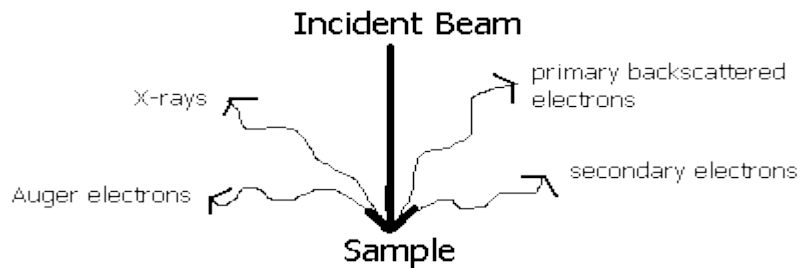


Figure 4.2 Interaction of electron beam with sample surface.

The emitted X-rays, secondary electrons and backscattered electrons are collected by detectors and then detectors send signals to the screen where final image is produced.



Figure 4.3 Photograph of Scanning Electron Microscope.

Particle size and morphology of as received powders (Silicon Carbide, alumina and cerium dioxide) were determined by scanning electron microscopy. Also to find the crack length scanning electron microscopy was performed. Images were taken at different magnifications.

4.2 Tumbler Mixer

It is a device which is used to mix powders, liquids homogeneously. Powder mixing is done in metallic vessel which is rotated by electric motor. Metallic vessel rotates on its horizontal axis with 100 rpm. Two type of mixing can be done by tumbler mixer i.e. wet mixing and dry mixing. Balls of hard material can be used to get homogeneity in less time period. Generally wet mixing is preferred than dry mixing because in dry mixing due to rubbing heat will produce and degradation of jar and balls may take place. For wet milling different liquids like acetone, benzene, toluene can be used. For the mixing of small amount of powder PVC bottles can be used. It is necessary to put PVC bottle at the center of drum.

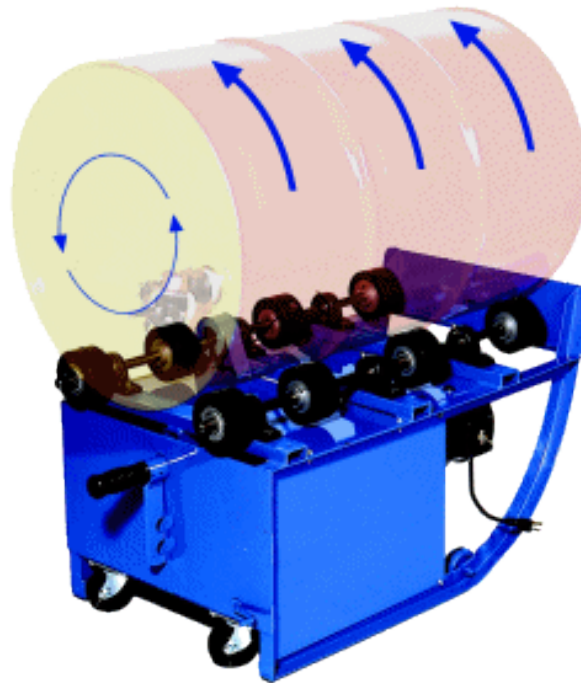


Figure 4.4 Tumbler Mixer.

To get homogenous mixture powders were mixed by tumbler mixer for 24 hours at 100 rpm. Wet mixing was done in acetone. Powder to ball ratio was 1:10. Different type of compositions were prepared (Table 4.1).

Table 4.1 Sample compositions prepared by tumbler mixing.

Sample Name	Composition (wt. %)	Rotational Speed (rpm)	Mixing Time (Hours)
C1	SiC-2Al ₂ O ₃	100	24
C2	SiC-2Al ₂ O ₃ -0.1CeO ₂	100	24
C3	SiC-2Al ₂ O ₃ -0.2CeO ₂	100	24
C4	SiC-2Al ₂ O ₃ -0.3CeO ₂	100	24
C5	SiC-2Al ₂ O ₃ -0.4CeO ₂	100	24
C6	SiC-2Al ₂ O ₃ -0.5CeO ₂	100	24
C7	SiC-2Al ₂ O ₃ -0.6CeO ₂	100	24
C8	SiC-2Al ₂ O ₃ -1CeO ₂	100	24

4.3 X-Ray Diffraction (XRD) Technique

It is an analytical method which is utilized in crystallography to identify various phases of crystalline material. Various information like size of unit cell (atomic spacing), crystal structure etc. can be gathered. XRD has three main components: Detector, X-Ray emitter and sample holder.

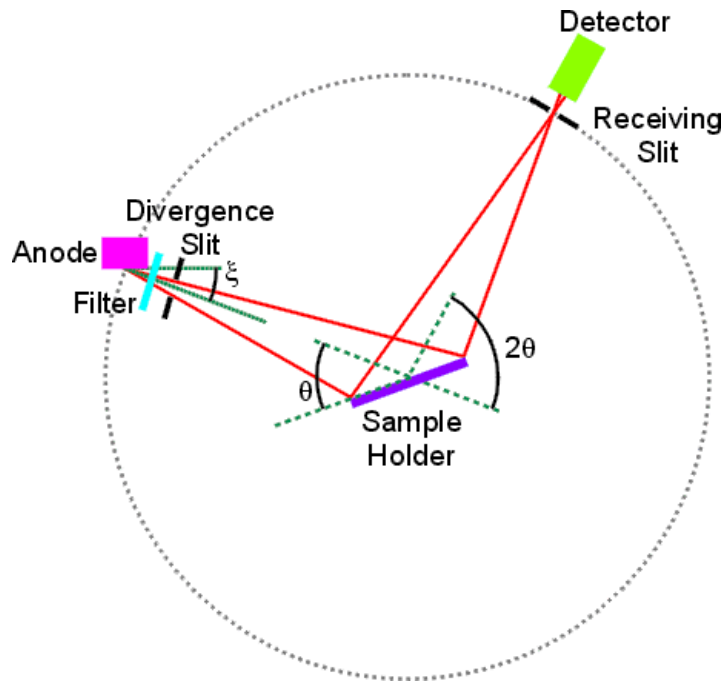


Figure 4.5 Schematic diagram of X-Ray Diffractometer.

To Calculate inter planer spacing Bragg's law is used. Bragg's law gives relationship between inter-planar spacing, angle of diffraction and wavelength.

$$n\lambda=2d \sin \theta$$

Where,

λ = Wavelength of electromagnetic radiation

d = Inter-planar spacing

θ = Angle of diffraction

Phase verification of the powders was done by X-Ray diffraction (XRD) (Smart Lab, Rigaku, Japan) using a $\text{CuK}\alpha$ line ($\lambda = 1.54 \text{ \AA}$), 40 kV and 30 mA. Diffraction patterns were collected at room temperature by rate $2^\circ/\text{min}$ in the 2θ range of $20^\circ - 80^\circ$.

4.4 Spark Plasma Sintering (SPS) Technique

It is advanced sintering technique in which high densification is achieved in very less time compared to conventional sintering. Sintering is activated by using electric current in spark plasma sintering. Current used by SPS is pulsed direct current because of this SPS is also recognized as PECS (pulsed electric current sintering) and FAST (field assisted sintering). It is a unique sintering process which is using ON-OFF DC current. Because of the frequent use of the ON-OFF DC current and voltage in powder materials, point of joule heating and spark discharge spreads in whole specimen. First commercialized SPS (DR. SINTER) was manufactured in Japan in the year 1990 from Sumitomo Coal Mining Co. Ltd.

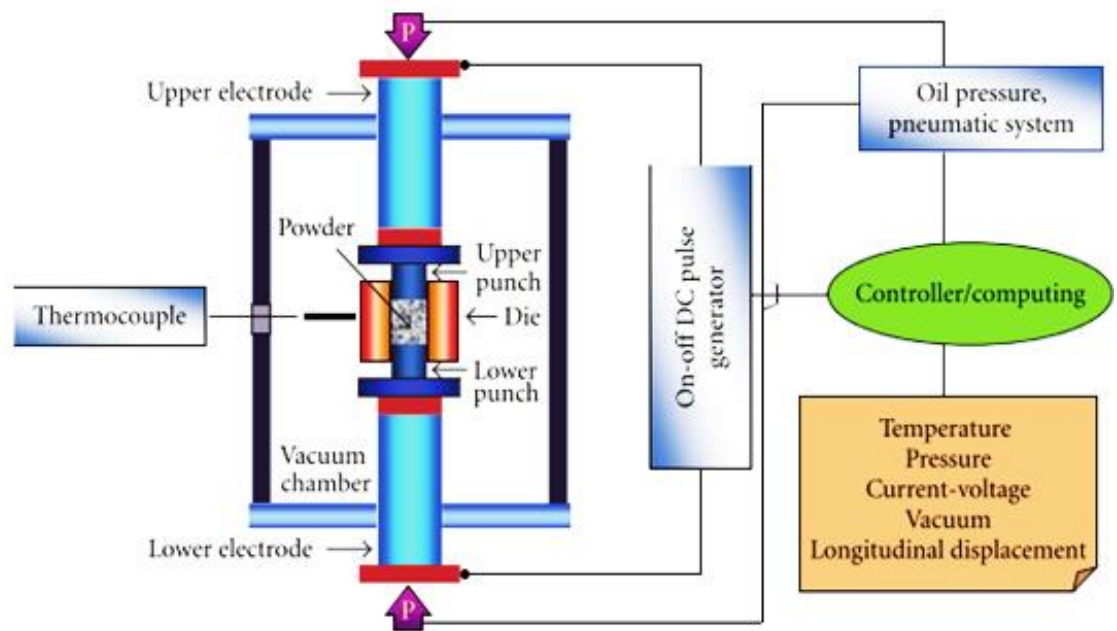


Figure 4.6 Schematic diagram of SPS[42].

SPS has a lot of advantages over conventional sintering processes, like pressure less sintering, hot-pressing, hot isostatic pressing and others, which are described as follows:

- Lower sintering temperature
- Shorter holding time, faster heating rates
- Marked comparative improvements in properties of materials consolidated by this method

Due to less holding time and application at Lower temperature. Relative density of Nano metric powders can be touched near to theoretical density with small grained microstructure [43]. The mentioned benefits make it a good candidate for sintering metal matrix nanocomposites (MMNC); sintering covalent ceramics such as Boron Carbide (B_4C) which usually require very high temperature of sintering; nanomaterial synthesis, preventing or at least minimizing grain growth to maintain the nanostructure features of the matrix [42]. It can also be used for diamond synthesis, biomaterials synthesis, Ti foam preparation etc.

During processing SPS undergoes Four main steps which are shown in figure 4.7. In first step gas is removed from chamber and vacuum is created. In next step pressure is applied and then joule (resistance) heating takes place and cooling takes place in final step.

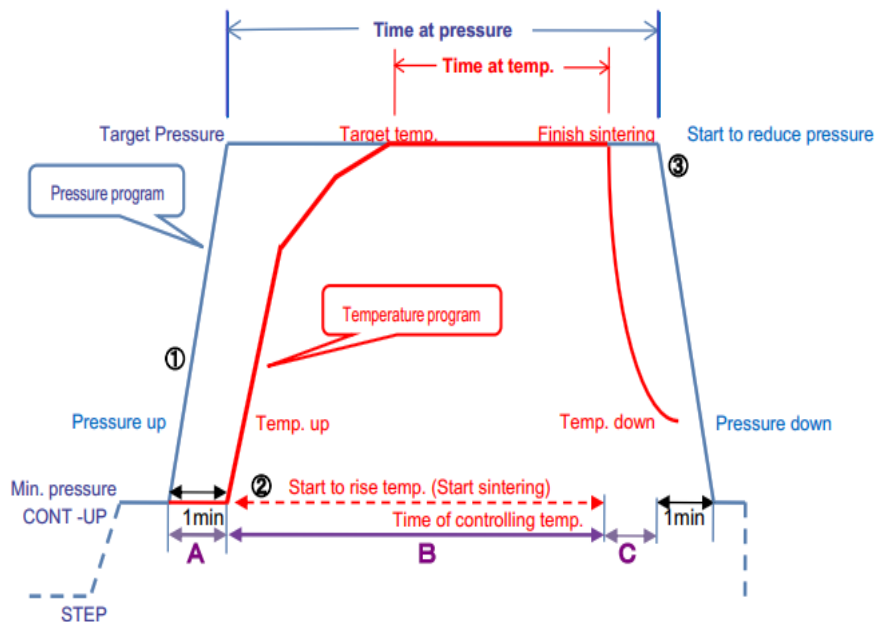


Figure 4.7 Stages of Spark Plasma Sintering [42].

First parameters were optimized by doing SPS on pure silicon carbide and then samples with different compositions were prepared by spark plasma sintering. All samples were prepared in 10 mm graphite dies. Table 4.2 gives the details of sintering parameters for different samples.

Table 4.2 SPS parameters for samples.

Sample Name	Composition (wt. %)	Sintering Temperature (°C)	Sintering Pressure (MPa)	Multistage
A	SiC	1800	50	No
B	SiC	1800	60	No
C	SiC	1600, 1800	60	Yes
D	SiC	1700, 1850	60	Yes
C1	SiC-2Al ₂ O ₃	1700, 1850	60	Yes
C2	SiC-2Al ₂ O ₃ -0.1CeO ₂	1700, 1850	60	Yes
C3	SiC-2Al ₂ O ₃ -0.2CeO ₂	1700, 1850	60	Yes
C4	SiC-2Al ₂ O ₃ -0.3CeO ₂	1700, 1850	60	Yes
C5	SiC-2Al ₂ O ₃ -0.4CeO ₂	1700, 1850	60	Yes
C6	SiC-2Al ₂ O ₃ -0.5CeO ₂	1700, 1850	60	Yes
C7	SiC-2Al ₂ O ₃ -0.6CeO ₂	1700, 1850	60	Yes
C8	SiC-2Al ₂ O ₃ -1CeO ₂	1700, 1850	60	Yes

4.5 Hardness Analysis

Hardness is very important property for a material. Ceramics are well known for their hardness. Hardness plays very important role to categories ceramics for different applications like dies and molds, seals, valves, ballistic armor, wear parts, erosive and abrasive parts, cutting tools etc.

To measure hardness for research purpose Vickers indentation method is generally used. For ceramic materials best quality diamond indenter is used. Samples are to be mounted on Vickers indenter and then indentations to be done on samples. Due to indentation square impression comes due to the square base pyramid. This impression is used by indenter to give hardness. Opposite faces of pyramid are separated by 136°. To calculate hardness following mathematical formula is used.

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

where

H_V = Vickers hardness Number

P = Load

L = Length of diagonals of indent impression

θ = Angle between opposite faces of indenter

Hardness of all samples was calculated at different loads with different loading and unloading rates with 10 sec dwell time by Vickers indenter (**Nanovea M1 Mechanical Tester, USA**). Radius of diamond indenter was 100 μm . Load for indentation was varied from 5 N to 50 N. At low load crack generation does not take place. For crack generation high load was used.

4.6 Fracture Toughness Analysis

Fracture toughness is also an important property for materials. It plays important role during the selection of material for design. It is represented by K_{IC} and it can be defined as the value of stress intensity factor at the tip of crack at which catastrophic failure takes place under uniaxial loading conditions.

Fracture toughness is calculated by indentation method. Due to indentation crack will generate. In 1976 Evan and Charles proposed a relation to find fracture toughness of materials tested by Vickers indenter.

$$K_{IC} = \frac{0.016H_V L^2}{c^{3/2}}$$

c = crack length from center of indent impression

L = Length of diagonals of indent impression

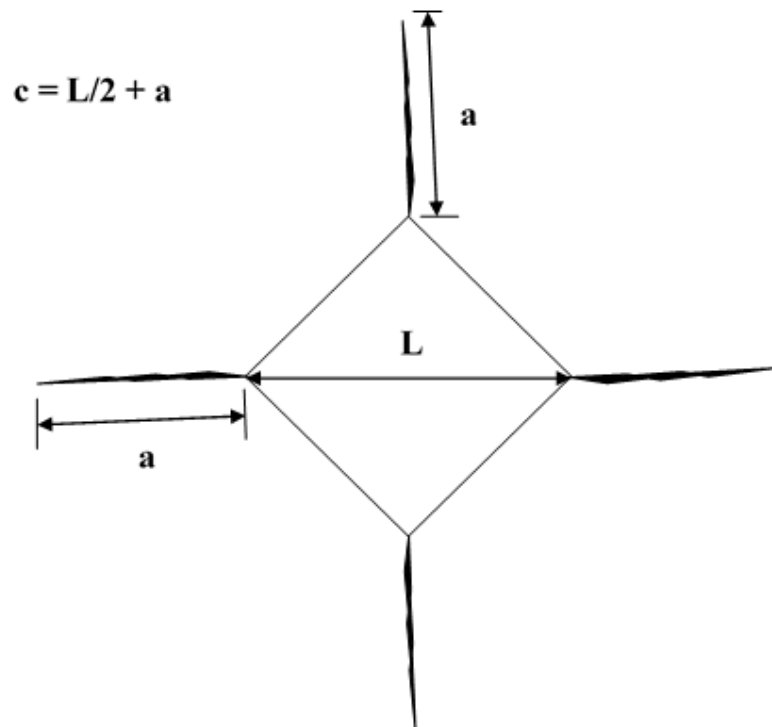


Figure 4.8 Formation of crack.

In 1981 Anstis et al. [44] modified that fracture toughness. They considered elastic modulus in equation an equation becomes

$$K_{IC} = 0.016 \sqrt{\frac{E}{H_V} \cdot \frac{P}{c^{3/2}}}$$

Where, E = Elastic modulus

P = Applied load

Fracture toughness of all samples were calculated at 15 N load. Crack length was measured by powerful microscope (Leica DMI5000M) and scanning electron microscope.

RESULTS AND DISCUSSION

5.1 Particle size calculations

Initially Scanning Electron Microscopy was performed to calculate the particle size of the powders.

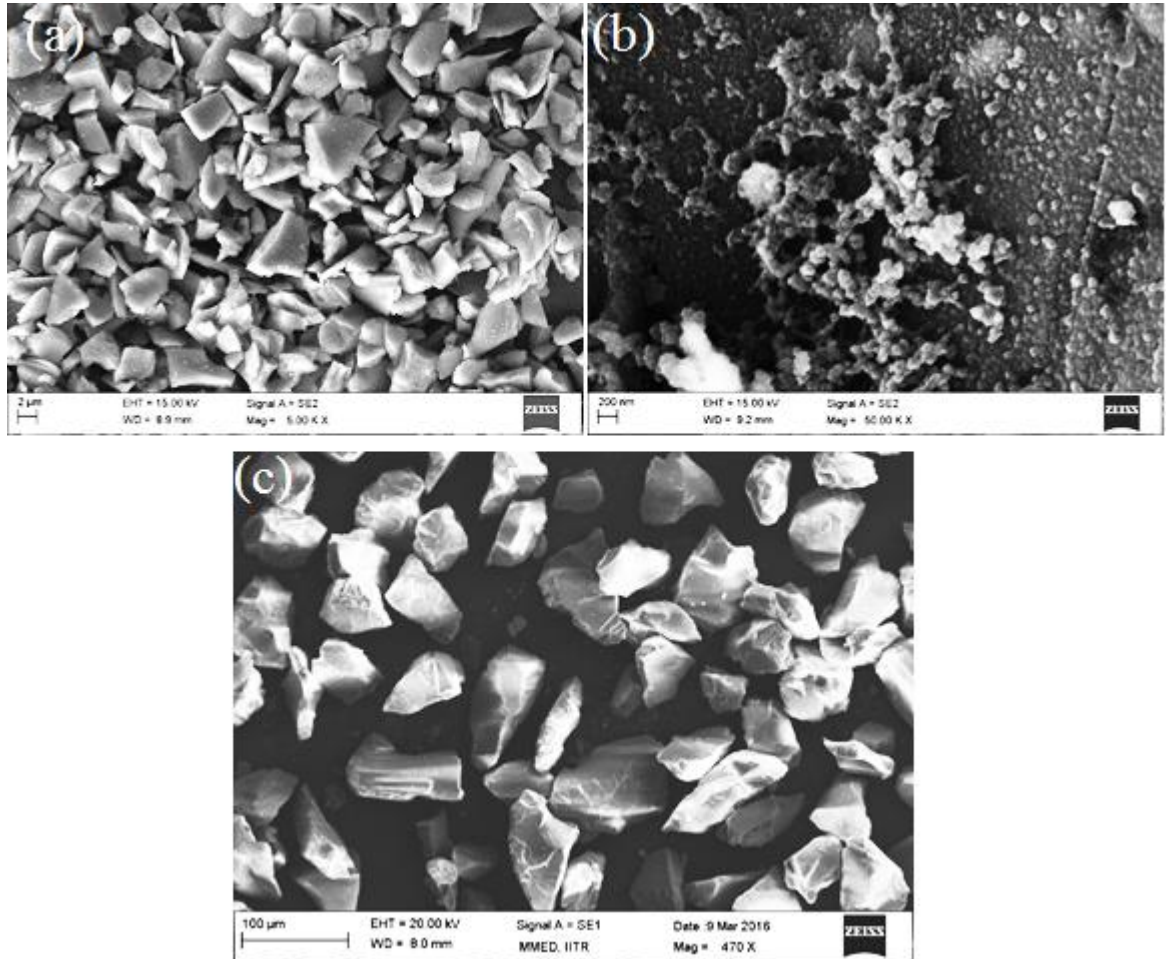


Figure 5.1 SEM images of (a) SiC, (b) CeO₂ and, (c) Alumina.

It was observed from scanning electron microscope that size of silicon carbide particles is around 5 μm, particle size of CeO₂ particles is around 60 nm and aluminium oxide have particle size around 65 μm.

5.2 Phase Analysis of Powder

After particle size calculations mixing of powders was done by tumbler mixture at 100 rpm. Then for phase analysis XRD was done. Few peaks appeared in XRD pattern which proves that some amount of ceria present in mixture. There is no other peak except silicon carbide, Alumina and ceria.

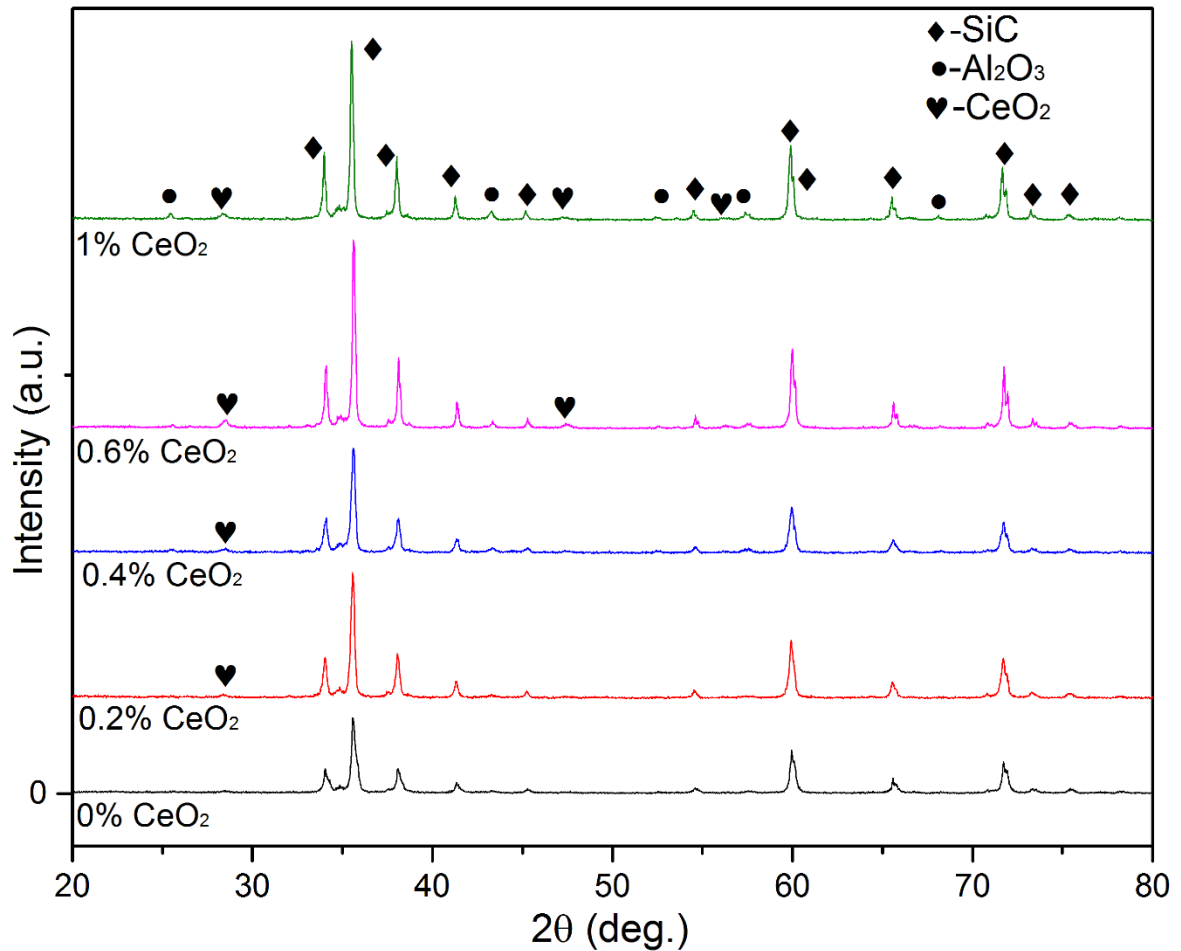


Figure 5.2 XRD Pattern of powder at different wt. % of CeO₂.

5.3 Densification

Densification of powder was done by spark plasma sintering. SPS is known for high densification but it is very difficult to achieve ~ 100 %. Efforts were made to get highest density for pure silicon carbide. At starting pure SiC powder was sintered at 1800 °C for 5 minutes at 50 MPa pressure. Relative density of sample was 77.24 % measured by Archimedes' principle. Displacement of punch in vertical direction was 2.73 mm.

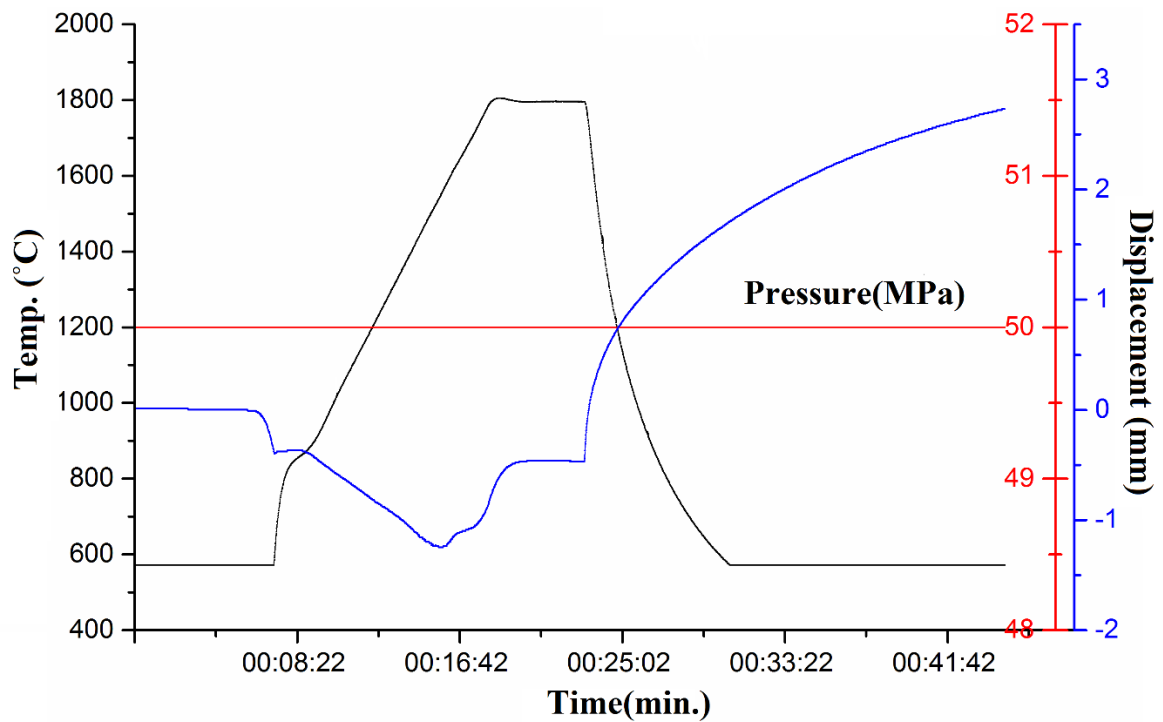


Figure 5.3 Temp. profile and change in displacement during sintering.

As relative density was too less then pressure was increased from 50 MPa to 60 MPa (maximum which can be applied in safety limit). During this time other parameters were same i.e. sintering temperature and holding time. Increment in density was measured but not exceptional. This time relative density was 79.61 %.

Now to get more densification next effort was made using multi stage sintering. This time two step sintering was used. Powder was first kept at 1600 °C for 4 min. after that temperature was increased to 1800°C and holed for 4 more minutes. Whole cycle ran under 60 MPa pressure.

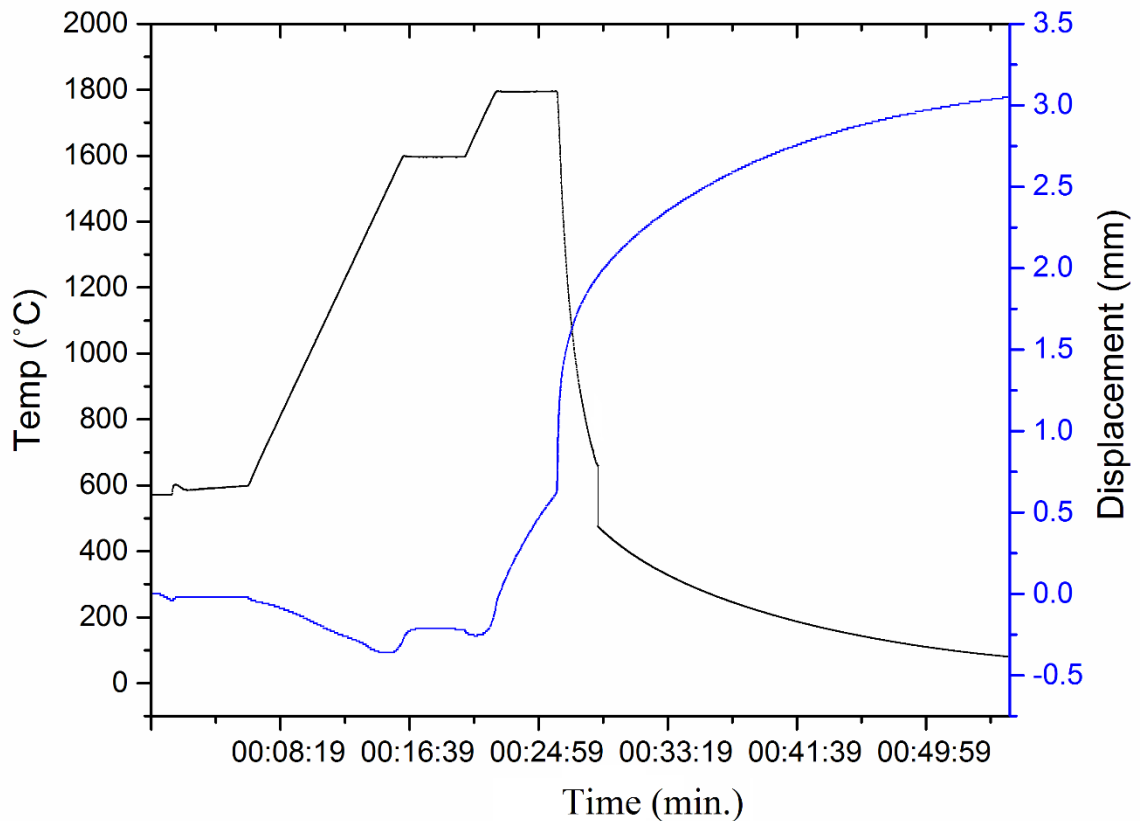


Figure 5.4 Temp. profile and change in displacement during multi stage sintering.

After multistage sintering Around 5 % of increment in density was observed. Relative density after this cycle was 84.38 %. Displacement of punch in vertical direction during sintering was 3.05 mm. Still density was not good then again cycle was changed to get more densification of powder. During last cycle, at 1st stage of sintering no vertical movement of punch was observed. vertical displacement of punch gives indication of densification. If vertical displacement is more than relative density will be high.

After that in next cycle temperature of 1st stage of sintering was increased by 100 °C and for 2nd stage it was increased by 50 °C. Holding time was 4 min. for first stage and 5 min. for second stage. Pressure during cycle was 60 MPa. After this only 2 % of increment in relative density was observed. Relative density was 86.42 % and vertical displacement of punch was 3.17 mm.

From the above efforts it was clear that fully dense samples cannot be prepared at low temperature. Then to achieve high density sintering additive was used. Very small amount (2 wt. %) of alumina was used. Due to sintering additive density was increased to ~98 %. Once density was achieved. All the samples were prepared on same cycle (Figure 5.5). Pressure for all cycles was 60 MPa.

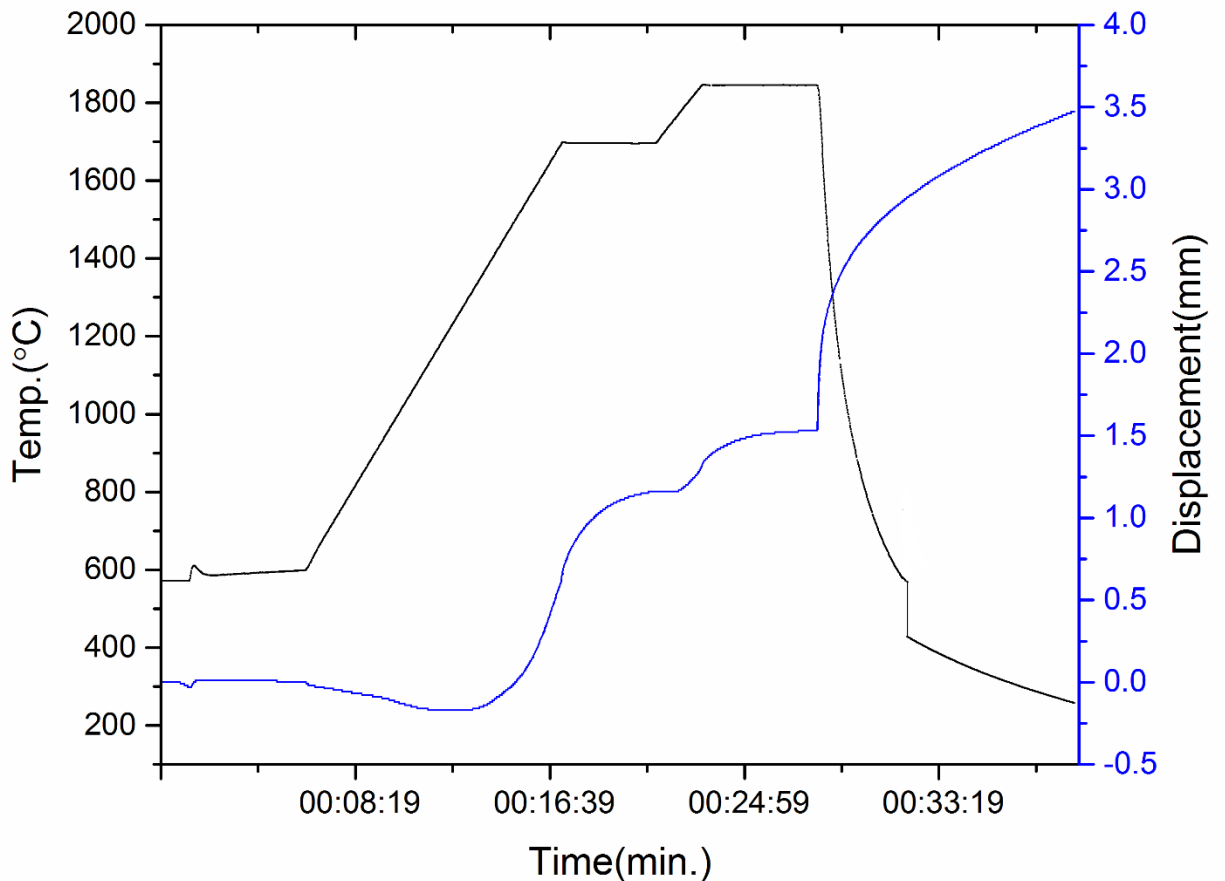


Figure 5.5 Temp. profile and change in displacement during multistage sintering at 60 MPa for sample using sintering additive.

By the help of sintering additive ~98 % relative density was attained. During sintering displacement of punch (Shrinkage) gives the indications about densification. It has direct relation with relative density. By measuring vertical movement of punch one can get idea of the relative density of sample during sintering. Total displacement of punch (shrinkage) includes powder shrinkage as well as contraction of graphite punch and electrodes. But contraction of electrode and punch can be neglected because sintering cycle for all cycles is same.

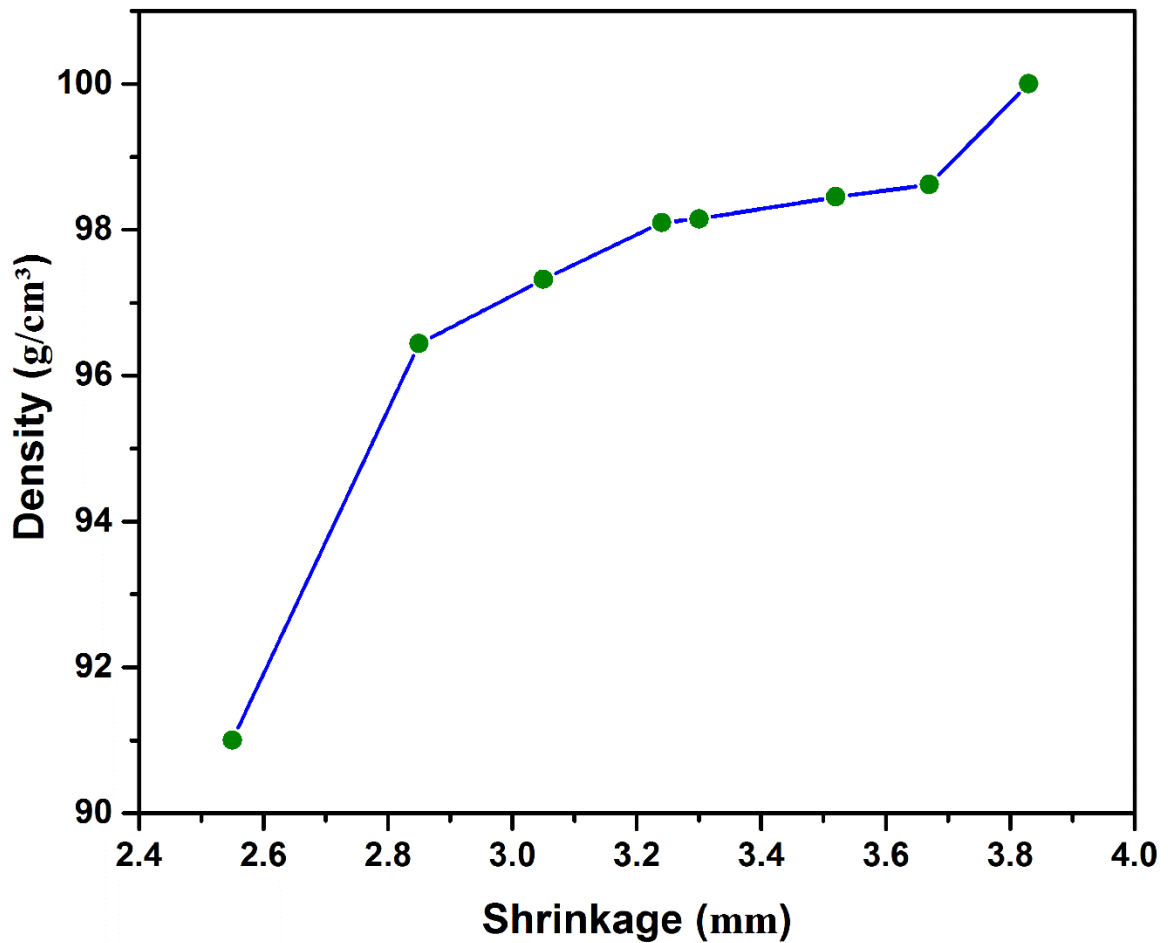


Figure 5.6 Density vs displacement of punch (Shrinkage).

5.3.1 Effect of ceria on relative density

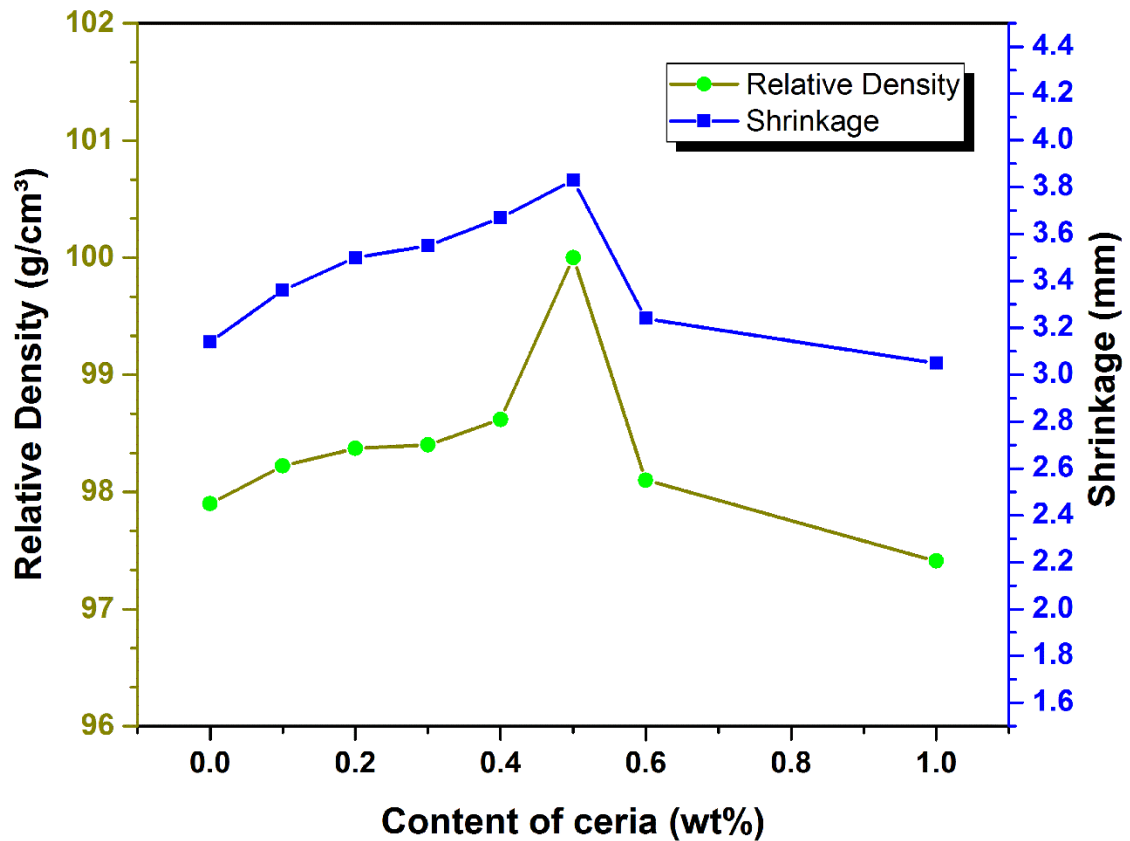


Figure 5.7 Effect of ceria on relative density and shrinkage.

As amount of ceria increases densification as well as displacement of punch increases till 0.5 wt. %. After 0.5 wt. % of ceria both densification and displacement of punch decreases. Maximum relative density ~100 % was achieved at 0.5 wt. % of ceria. Till 0.5 wt. %, CeO₂ supports densification of silicon carbide after 0.5 wt. %, CeO₂ shows reverse effect on densification. It may be because for this composition main reason for densification is lattice diffusion from grain boundary of alumina and extra amount of CeO₂ is reducing flowability of alumina. Due to this densification is reducing.

5.4 Phase Analysis of Sintered Samples

Figure 5.8 shows the XRD analysis of sintered samples at different content of cerium dioxide. It was found that at 0 wt. % CeO_2 second phase formation took place. From figure it can be seen that at 0 wt. % CeO_2 peaks related to mullite and aluminium silicate came in picture. It means at 1850 °C reaction is taking place between alumina and silicon carbide. But when cerium dioxide was added then peaks related to aluminium silicate phase did not come. It can be assumed that cerium dioxide is restricting the formation of aluminium silicate. More research is required to know the mechanism behind this. Till 0.5 wt. % of CeO_2 peaks related to alumina does not appear but after 0.5 wt. % ceria, alumina peak appears and intensity of mullite peaks decreases.

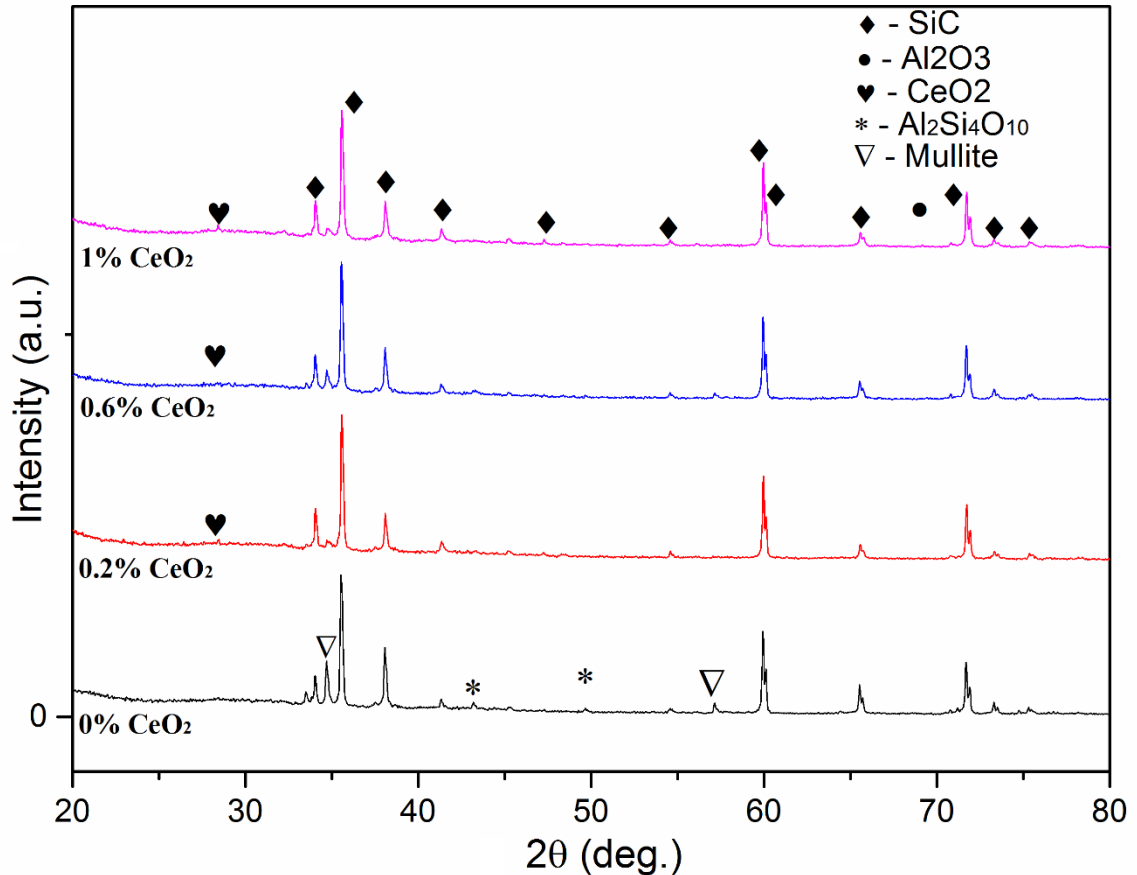


Figure 5.8 XRD Pattern after sintering at different wt. % of CeO_2 .

5.5 Microstructure

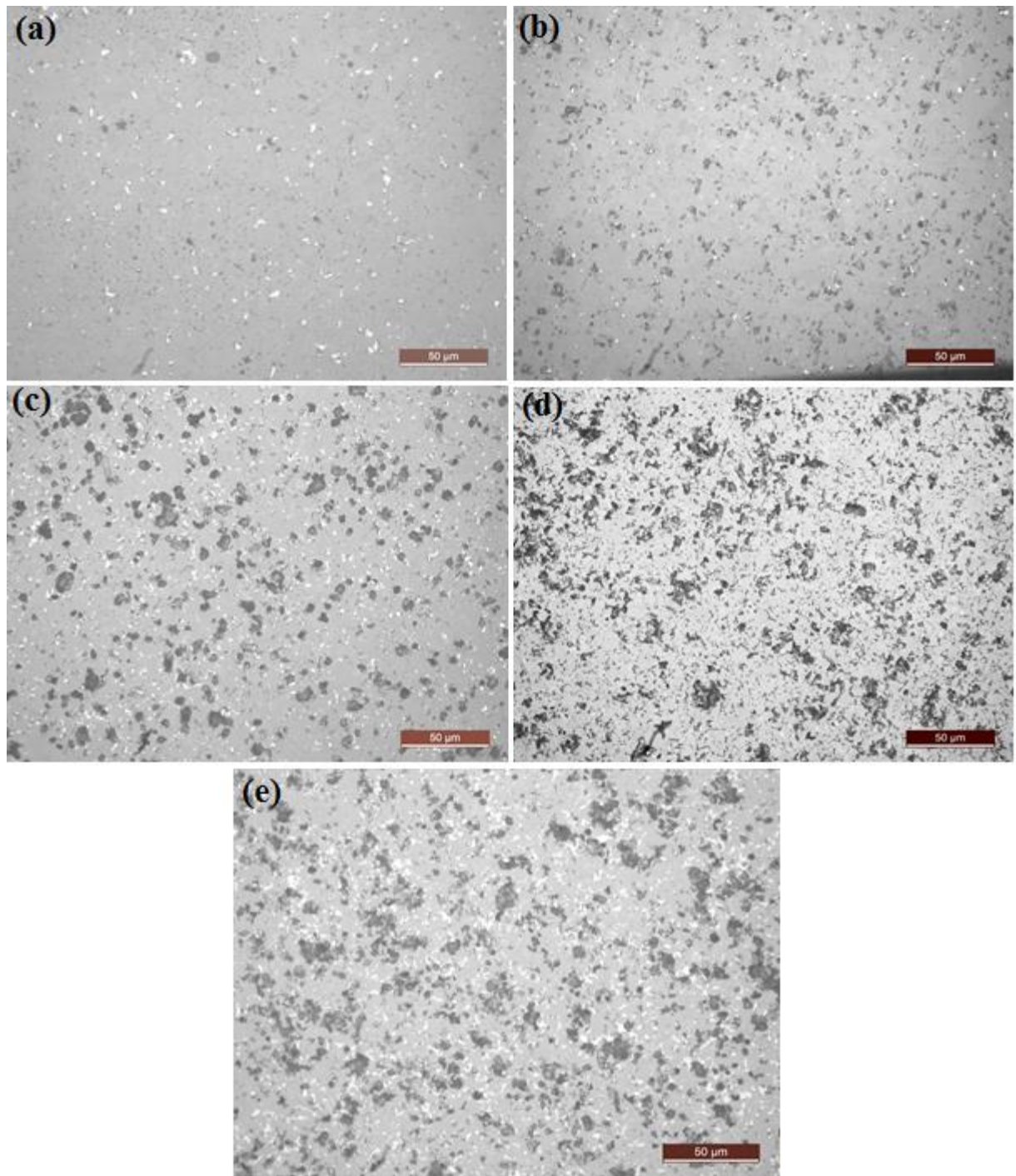


Figure 5.9 Polished surface of samples at different content of CeO₂ (a) 0 % CeO₂, (b) 0.1 % CeO₂, (c) 0.2 % CeO₂, (d) 0.5 % CeO₂, (e) 1 % CeO₂.

As there is difference in coefficient of thermal expansion of all three materials. Due to this thermal stress generation taking place in the composite.

Table 5.1 Coefficient of thermal expansion.

Sr. no.	Material	Coefficient of thermal expansion ($10^{-6}/^{\circ}\text{C}$)
1	SiC	4
2	Al ₂ O ₃	8.1
2	CeO ₂	29.2

The difference in coefficient of thermal expansion of silicon carbide and cerium dioxide is too high due to this difference thermal stress generation is also when cerium dioxide comes in composite. Figure 5.9 is showing the images of polished surface. It can be seen that with the increase in CeO₂ content black part in images increases. Black part is showing the portion from where material is pulled out during polishing. Pulling out of material is due to thermal stresses. In figure 5.9(a) black portion is very less because difference in coefficient of thermal expansion of silicon carbide and alumina is less. Due to this less thermal stresses are generated and less material is pulled out during polishing. But as cerium dioxide comes in composite more thermal stresses are generated and more material is pulled out from surface. It can be easily seen that as content of cerium dioxide increases in composite, black part is increasing.

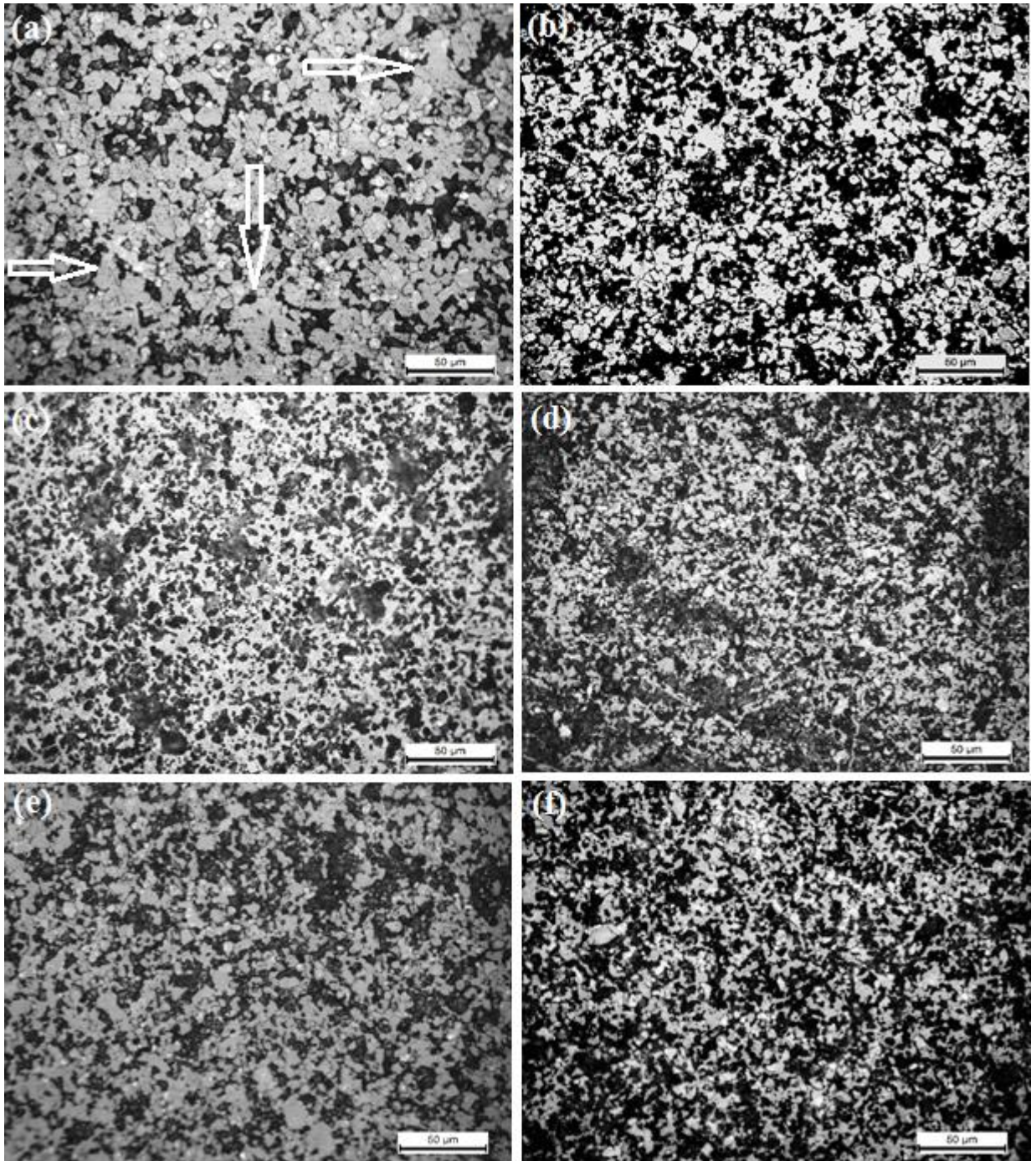


Figure 5.10 Microstructure of sample with composition (a) 0 wt. % CeO₂, (b) 0.1 wt. % CeO₂, (c) 0.2 wt. % CeO₂, (d) 0.5 wt. % CeO₂, (e) 0.6 wt. % CeO₂, (f) 1 wt. % CeO₂.

Due to addition of cerium dioxide grain growth is restricted. Abnormal grain growth can be seen from microstructure of sample in which cerium dioxide is not added. Figure 5.10(a) is showing the microstructure of sample without ceria content. In figure 5.10(a) abnormal grain growth can be seen arrows are showing abnormal grain growth. But after addition of ceria no abnormal grain growth took place because particle size of ceria is very small so surface of ceria has more no. of oxygen vacancies. Due to this surface of cerium dioxide particles becomes more reactive. These reactive particles of cerium dioxide are dispersed at the interaction of silicon carbide and liquid alumina phases which reduces surface energy by making bonds with silicon carbide and alumina. As surface energy of silicon carbide particles decreases then possibility to join particles during sintering decreases. This is how grain growth restriction takes place due to addition of nano cerium dioxide particles. Grain size was measured by line intercept method. Average grain size of the sample without ceria was around 12 micrometers. After addition of 0.1 wt. % of ceria average grain size was reduced to around 8.65 micrometers. Around 28 % of decrement was measured. Further addition of cerium dioxide is not showing too much effect on grain size. Addition of cerium dioxide more than 0.1 wt. % is not beneficial for microstructure.

5.6 Hardness

Hardness of all samples was measured at 15 N load. Figure 5.10 shows load vs depth curve by which hardness was measured during loading and unloading. Rate of loading and unloading was 15 N/min. This curve also gives the indication about the elasticity and plasticity of the material.

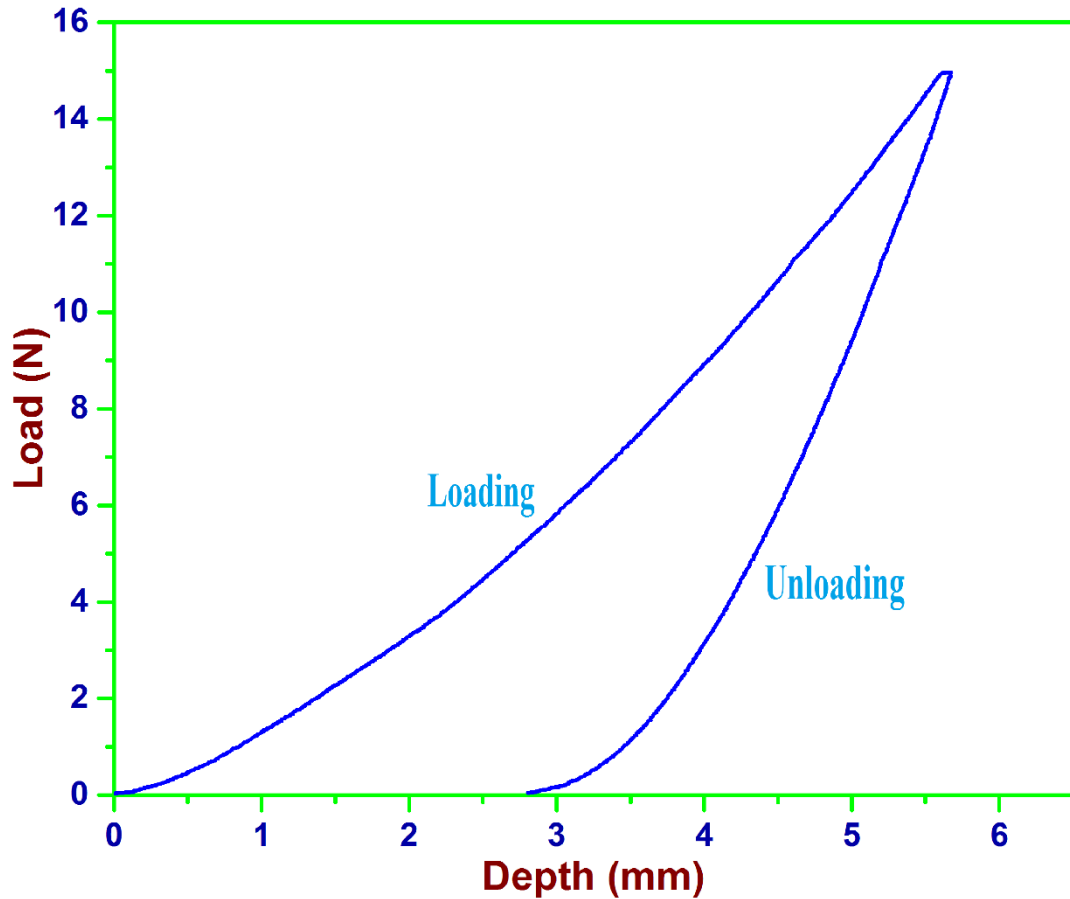


Figure 5.11 Load vs depth curve during indentation.

Figure shows the effect on hardness due to addition of CeO_2 . Hardness of sample increases from 2057 kg/mm^2 to 2323 kg/mm^2 due to addition of cerium dioxide. This increment in hardness is due to reduction in grain size. Cerium dioxide acts as grain growth inhibitor. Around 12.9 % of increment in hardness is measured at 0.1 wt. % of ceria.

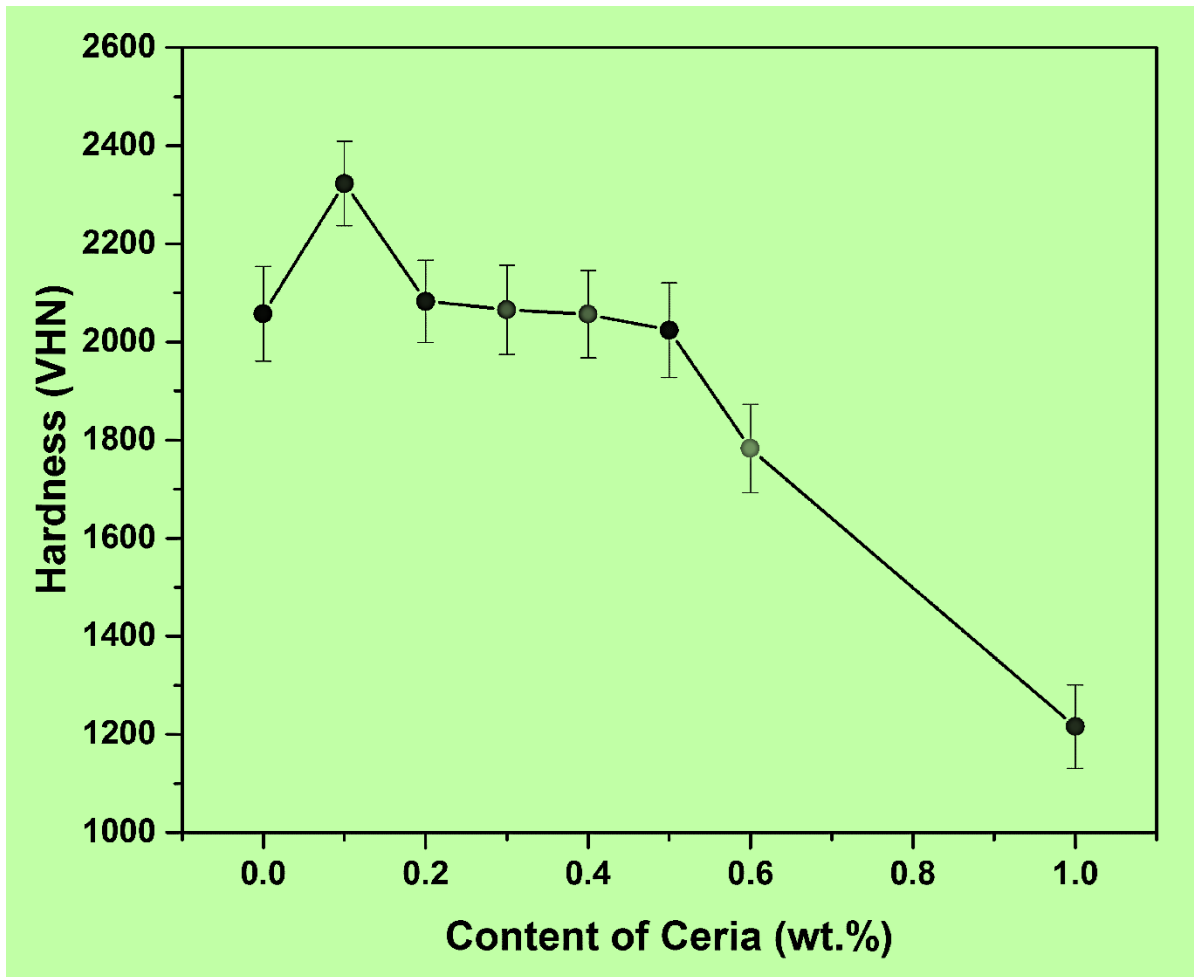


Figure 5.12 Effect of ceria on Hardness.

Hardness of pure silicon carbide samples which are not fully dense was also measured. As these samples has porosity around 20 % due to this very low hardness was shown by these samples.

Table 5.2 Hardness of samples at different compositions.

Sr. No.	Sample	Composition (wt. %)	Hardness (VHN)
1	A	SiC	728.4 ± 42.36
2	B	SiC	845.7 ± 38.23
3	C	SiC	893.8 ± 40.91
4	D	SiC	954.3 ± 43.22
5	C1	SiC-2Al ₂ O ₃	2057.2 ± 96.27
6	C2	SiC-2Al ₂ O ₃ -0.1CeO ₂	2323 ± 85.73
7	C3	SiC-2Al ₂ O ₃ -0.2CeO ₂	2082.8 ± 83.84
8	C4	SiC-2Al ₂ O ₃ -0.3CeO ₂	2065.9 ± 91.01
9	C5	SiC-2Al ₂ O ₃ -0.4CeO ₂	2056.3 ± 89.07
10	C6	SiC-2Al ₂ O ₃ -0.5CeO ₂	2023.9 ± 96.42
11	C7	SiC-2Al ₂ O ₃ -0.6CeO ₂	1783 ± 90.13
12	C8	SiC-2Al ₂ O ₃ -1CeO ₂	1215.8 ± 84.88

After 0.1 wt. % of ceria hardness starts decreasing because amount of soft phase is increasing in matrix and there is no further decrement in grain size due to addition of CeO₂. Decrement in hardness from 0.2 wt. % of CeO₂ to 0.5 wt. % CeO₂ is almost negligible. Because there are two opposite phenomenon working together, one is densification and other is increment of content of soft phase. Till 0.5 wt. % of CeO₂ densification of sample increases due to this hardness increases and due to increment in content of soft phase hardness decreases. Effect of these two phenomenon is canceling each other due to this very small decrement is observed. but after 0.5 wt. % CeO₂ these two phenomenon starts supporting each other (densification is decreasing and content of soft phase is increasing). Due to this abrupt change in hardness is measured after 0.5wt. % of CeO₂.

5.7 Fracture Toughness

Fracture toughness of all the samples is measured by using crack length. Cracks were generated by indentation at load 15 N. Figure 5.13 and 5.14 shows initiation of crack from all corners of indent.

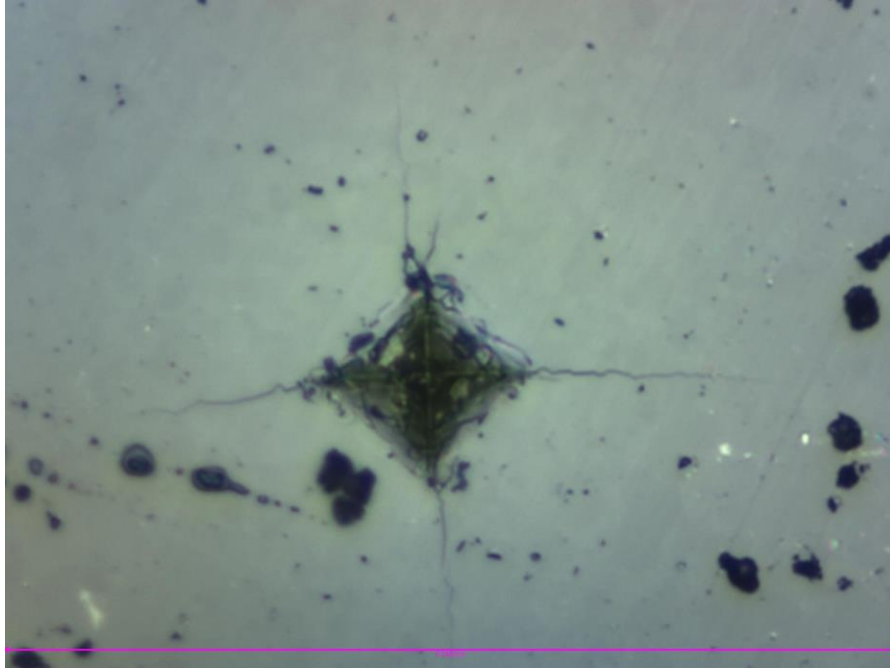


Figure 5.13 Crack initiation due to indentation without ceria addition.

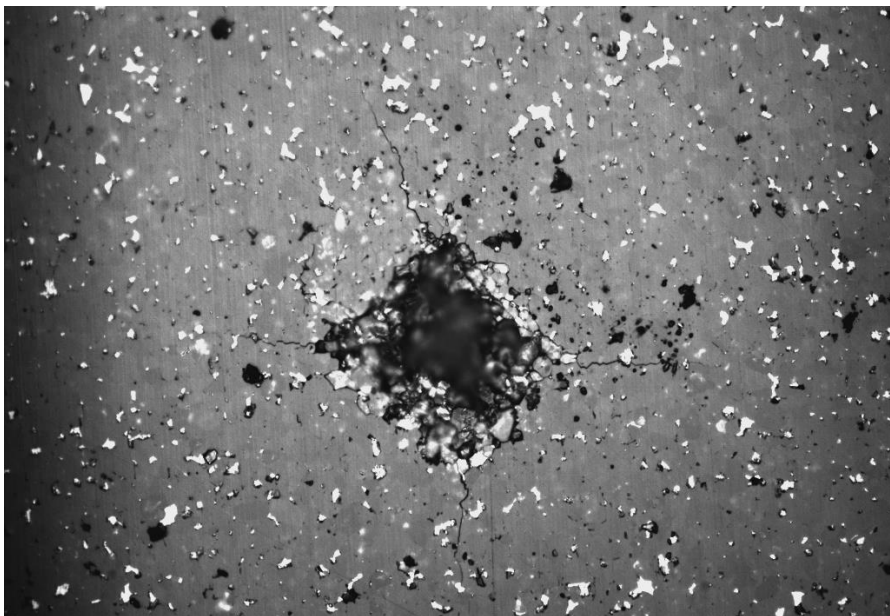


Figure 5.14 Crack initiation due to indentation with 0.1 wt. % ceria.

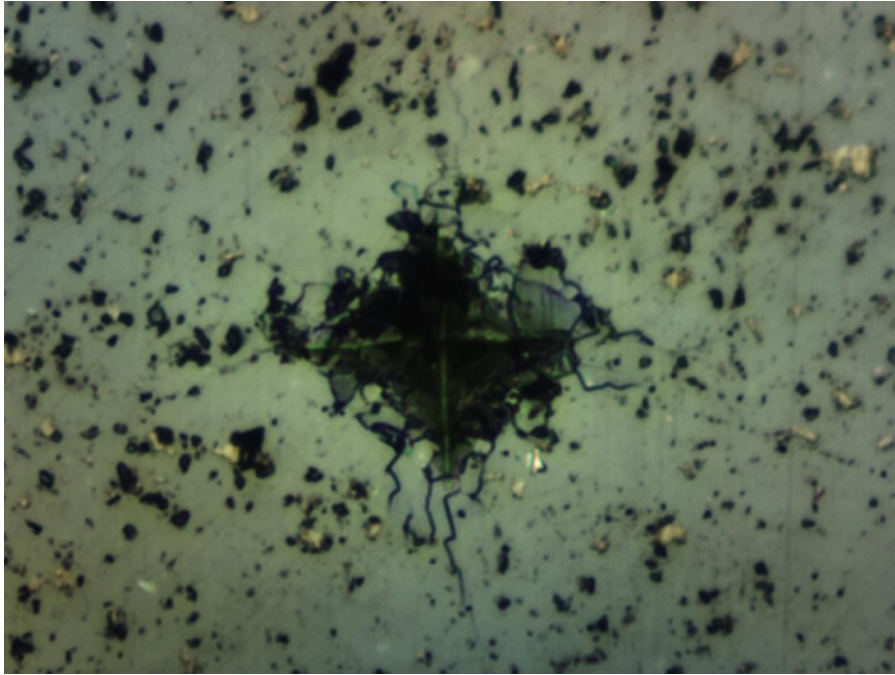


Figure 5.15 Crack initiation due to indentation with 0.5 wt. % ceria.

Figure 5.11, 5.12 and 5.13 shows crack initiation due to indentation at 0, 0.1 and 0.5 wt. % of CeO_2 . It can be clearly seen that when ceria is not present in composite then crack is propagating to a long distance and only on few places crack deflection can be seen. But when we see crack at 0.1 wt. % of ceria, it is observed that crack propagation is different and crack deflection can be clearly seen at many places. When content of ceria increased to 0.5 wt. % then a mixed type of fracture comes in picture and crack deflection and crack bridging can be noticed easily. Crack length of all samples was measured by high power microscope. By using crack length, hardness and elastic modulus, fracture toughness was calculated which is shown in figure 5.16.

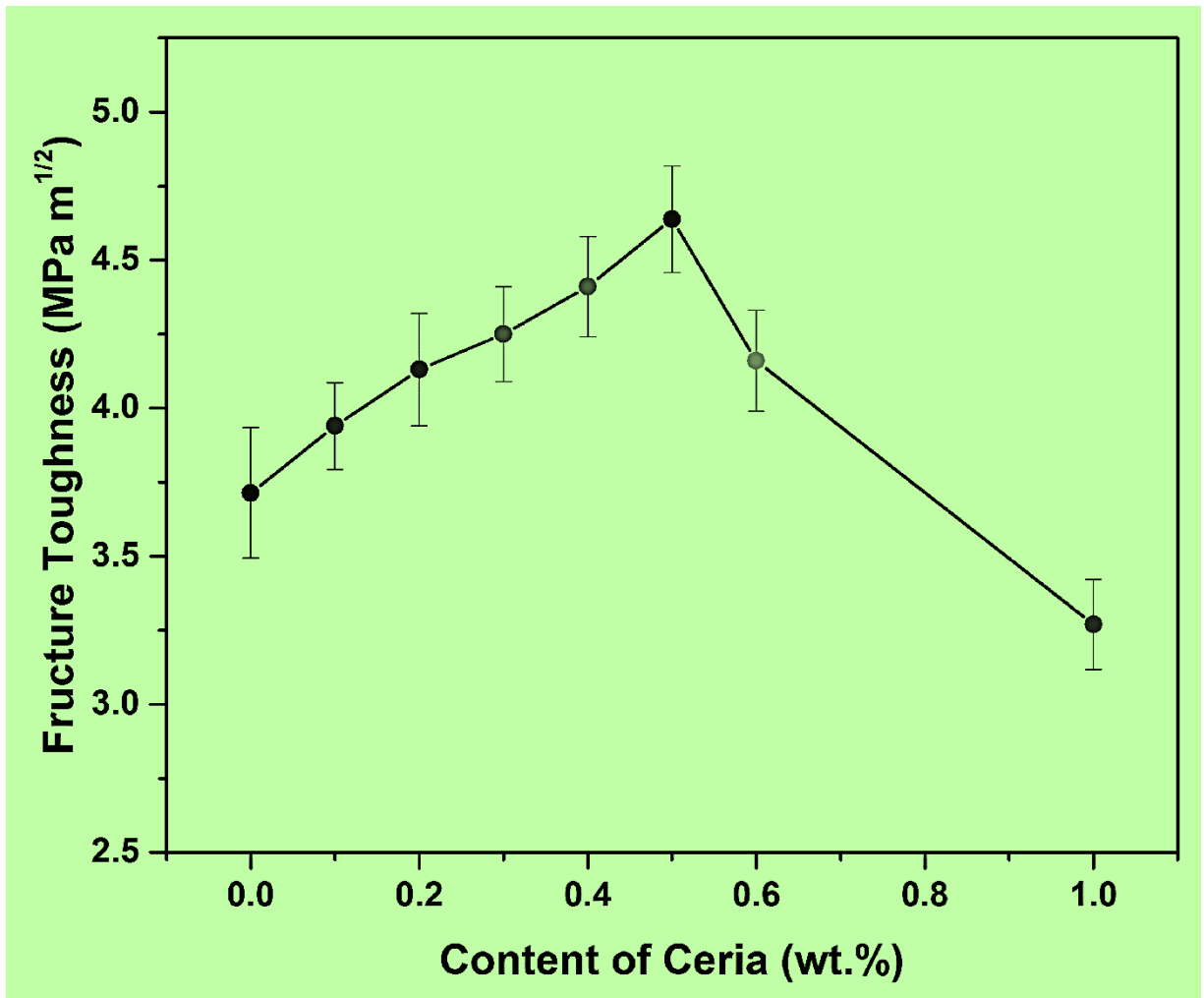


Figure 5.16 Effect of ceria on fracture toughness.

Fracture toughness of composite without ceria addition was 3.71 MPa m^{1/2}. After addition of cerium dioxide, it continuously increases to 4.64 MPa m^{1/2} till content of ceria reaches to 0.5 wt. %. after that fracture toughness starts decreasing and it decreases to 3.27 MPa m^{1/2} when content of ceria reaches to 1 wt. %. It may be due to second phase coarsening. After optimum size it is not deflecting crack but allowing through inside. Due to this fracture toughness is decreasing.

Table 5.3 Fracture Toughness of samples at different composition of CeO₂.

Sr. No.	Sample	Composition (wt. %)	Fracture Toughness (MPa m^{1/2})
1	C1	SiC-2Al ₂ O ₃	3.71 ± 0.22
2	C2	SiC-2Al ₂ O ₃ -0.1CeO ₂	3.94 ± 0.15
3	C3	SiC-2Al ₂ O ₃ -0.2CeO ₂	4.13 ± 0.19
4	C4	SiC-2Al ₂ O ₃ -0.3CeO ₂	4.25 ± 0.16
5	C5	SiC-2Al ₂ O ₃ -0.4CeO ₂	4.41 ± 0.18
6	C6	SiC-2Al ₂ O ₃ -0.5CeO ₂	4.64 ± 0.17
7	C7	SiC-2Al ₂ O ₃ -0.6CeO ₂	4.16 ± 0.17
8	C8	SiC-2Al ₂ O ₃ -1CeO ₂	3.27 ± 0.15

This 25 % increment in fracture toughness is due to following phenomenon: -

- Crack deflection and bridging by grain boundary
- Crack deflection and bridging by secondary phase
- Nano crack formation around crack tip

As grain size is reducing then grain boundary region is more due to more grain boundary region possibility of crack deflection and crack bridging from grain boundary is high and crack is not able to propagate to a long distance. as a result, fracture toughness is increasing.

Crack deflection by second phase was also seen by scanning electron microscope figure 5.16. arrows are showing crack deflection and crack bridging by second phase. Due to crack deflection and bridging by second phase or grain boundary, crack losing its severity and traveling distance is decreasing. Due to this fracture toughness.

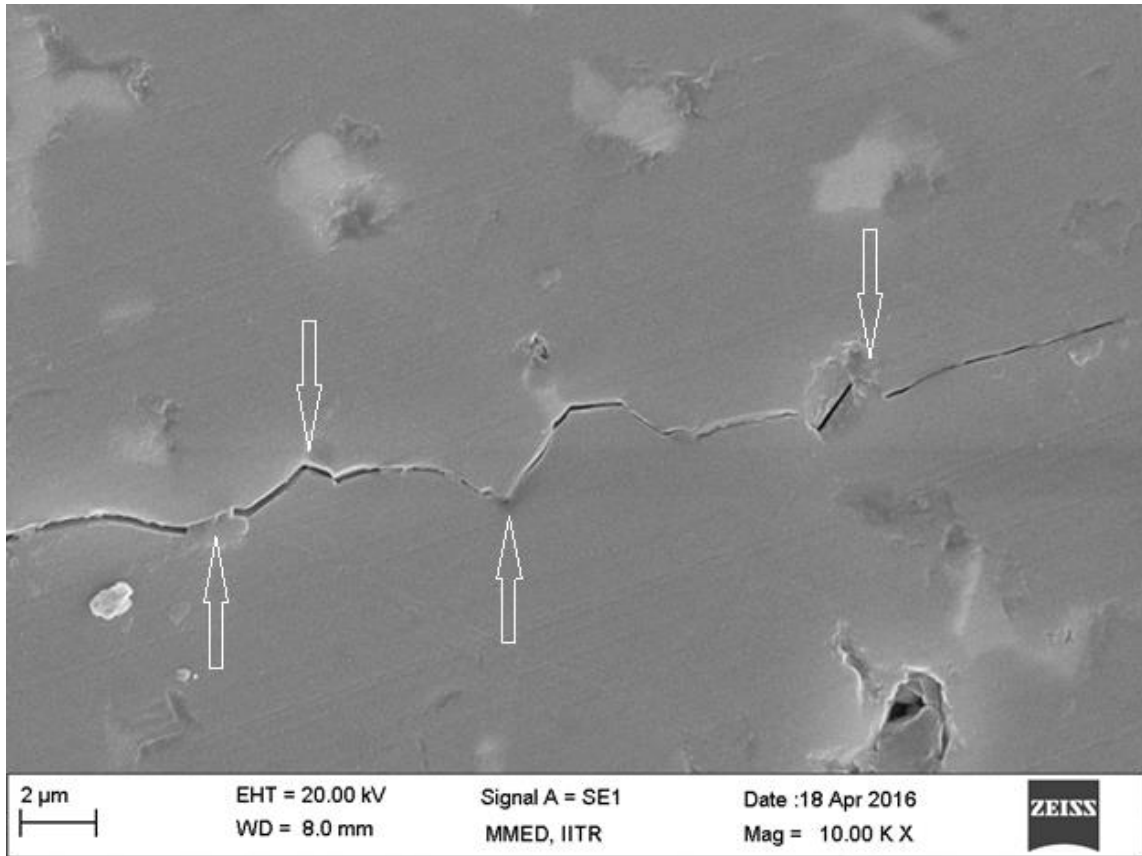


Figure 5.17 Crack defection and crack bridging by second phase.

It may also be possible that due difference in coefficient of thermal expansion, very small cracks similar to dislocation are generating at the surface of cerium dioxide because size of cerium dioxide is very small and due to these nano cracks fracture process zone strengthening is taking place. Due to fracture process zone strengthening fracture toughness is increasing. More work is required to find the presence of this phenomena.

CHAPTER 6

SUMMARY

The whole study was about the methods to improve the toughness of ceramics composites and decrease the sintering temperature. Reducing particle size, introduction to second phase by liquid phase sintering and solid phase sintering with sintering additives are the different approaches which were used. By reducing particle size micro crack toughening takes place during micro crack toughening fracture process zone strengthening takes place. In introducing second phase by liquid phase sintering, diffusion rate is fast and higher density of ceramics can be achieved. Second phase formation takes place during liquid phase sintering deflects cracks. In this type of sintering fracture toughness and strength increases and corrosion resistance, hardness and sintering temperature. Introducing second phase by solid phase sintering is done to increase fracture toughness and strength without decreasing hardness and corrosion resistance.

- To densify powder spark plasma sintering technique was used. Density near to theoretical density was achieved after using alumina as sintering additive. Samples were prepared using 10 mm diameter die-punch at 1850 °C and 60 MPa pressure with different compositions of CeO₂.
- Hardness and fracture toughness of samples was measured by indentation method at 15 N load.
- Increase in hardness was 12.9 % at 0.1 wt. % cerium dioxide. After 0.1 wt. % hardness decreases due to increase in content of soft phase.
- Around 25 % improvement in fracture toughness was measured after addition of 0.5 wt. % cerium oxide powder due to restriction in grain growth due to nano sized CeO₂ particles After 0.5 wt. % cerium oxide density and fracture toughness decreased.

CHAPTER 7

SCOPE FOR FUTURE WORK

Silicon carbide based composites are very useful in structural applications. Due to ceria addition mechanical properties of silicon carbide are increasing but brittleness is present. As addition of ceria was a fresh attempt to increase the properties of silicon carbide. Many points are yet to be revealed. Characterization of second phases which are forming during sintering is left. Characterization and Effect of second phases on mechanical properties can be studied. Effect Thermal stresses which are generating due to difference in thermal coefficient of expansion can also be studied. More efforts can be made to know the actual reasons for few points. Other materials by which reduction in brittleness takes place can be used with this composite and more improvement in mechanical properties can be measured.

CHAPTER 8

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