

**GELCASTING OF ALUMINA AND
ALUMINA-cBN USING 2-HYDROXYETHYL
METHACRYLATE AS MONOMER**

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**A dissertation submitted to the Faculty of Engineering and the Built
Environment, University of the Witwatersrand, Johannesburg, in fulfilment
of the requirements for the degree of Master of Science in Engineering.**

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DECLARATION

I declare that this disseratation is my own, unaided work. It is being submitted for the Degree of Master of Science in Engineering in the University of Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination in any other University.

(Signature of candidate)

----- day of-----2008

ABSTRACT

Gelcasting is a promising technology for manufacturing of advanced structural ceramic components. This forming process was developed to overcome some of the limitations of other complex-shape forming techniques such as injection molding and slip casting. Gelcasting is a new near net shaping technique, which has rapidly evolved from a laboratory invention towards industrial application. In this work, a highly loaded but very fluid slurry consisting of ceramic powder (Al_2O_3 , $\text{Al}_2\text{O}_3\text{-cBN}$), water, dispersant (Ammonium poly acrylic acid) and gelformer (2-hydroxyethyl methacrylate), is poured into a mold and subsequently gelled. Once gelation has taken place, the part is strong enough to retain its shape and can be demolded, dried, calcined and sintered. The industrialization of gelcasting technique has been prevented to some extent because the main component of the gel, acrylamide, is a neurotoxin. Therefore a low-toxicity gel casting system is highly more desirable in this field. Feasibility of using a non-toxic gel-former (2-hydroxyethyl methacrylate) is studied. Relevant processing parameters such as slurry composition, slurry rheology and preparation procedures, de-airing under vacuum with addition defoaming agents, drying under controlled temperature and humidity conditions and gelation schedules were studied along with results of sintering in air at 1450°C of alumina gelcast and sintering under argon at 1450°C of alumina-cBN gelcast and resulting properties and microstructures.

This dissertation is dedicated to
My late father Donatien Bantshi
My mother Lucie Kwetengata
My wife Viviane Kitenge
and my son Ephraim Bantshi

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LIST OF ABBREVIATIONS AND SYMBOLS

APAA	=	ammonium poly(acrylic acid)
APS	=	ammonium persulfate
HEMA	=	2-hydroxyethyl methacrylate
BN	=	boron nitride
cBN	=	cubic boron nitride
MBAM	=	methyl bisacrylamide
GPa	=	gigapascal
h	=	hour
min	=	minute
Pa	=	pascal
PVP	=	polyvinyl pyrrolidone
s	=	second
RH	=	relative humidity
SEM	=	scanning electron microscopy
TEMED	=	tetramethylethylenediamine
TGA	=	thermal gravimetric analysis
XRD	=	X-ray diffraction
μm	=	micron
γ	=	shear rate
ζ	=	zeta-potential

CHAPTER 1 INTRODUCTION

During recent years it has been demonstrated that colloidal fabrication methods for ceramics have many advantages over dry-processing methods. These advantages are realized by controlling and manipulating the forces between the particles in suspension in a liquid. The manufacture of slurries used in wet-processing routes (slip, pressure and gel casting, injection moulding, etc.) offers the opportunity of breaking up undesirable powder agglomerates by milling or ultrasonic treatment or of removing them completely by filtration or sedimentation. Therefore, flaw size can be minimized and optimal particle packing and homogeneous green microstructures can be obtained.

Emphasis will be placed on gelcasting as colloidal processing techniques which have been suggested as a method for preparing advanced ceramic materials with improved mechanical properties. Weakly bound agglomerates such as those held together by Van der Waals forces are broken apart with dispersion and mixing techniques such as ultrasound and ball milling, and strongly bound agglomerates can subsequently be removed by either sedimentation or filtration. The resulting dispersed slurry can be consolidated into a relatively dense green body with only small inhomogeneities.

Dispersion was optimized initially for the pure alumina powders and subsequently for the composite slurries alumina-cBN. The resulting systems were fully characterized and then formed using the gelcasting technique and finally sintered at temperature of 1450° C using pressureless sintering. The sintered compacts were characterized based on density measurements, microstructural analysis and hardness measurements. Relevant literature on colloidal processing methods, rheology of suspensions and slurries and forming methods is discussed in chapter 2 of this dissertation. Chapter 3 gives details about experimental procedures used, problems encountered when using these techniques, and apparatus used. Chapter 4

gives an in-depth discussion of the results. Conclusions and findings drawn from the results are presented in chapter 5.

The nature of this work involves using alumina and other materials to form compacts through gelcasting. Interparticle forces in these systems are controlled by the use of surface active processing chemicals. In order to make ceramic materials, powder compacts have to be sintered, the driving force for sintering being the reduction of surface energy. For many applications in ceramic processing it is desirable to sinter at relatively low temperatures and to obtain fully dense and fine-grained microstructures. The driving force and efficiency of sintering is influenced by the basic powder properties such as purity, grain size and chemical homogeneity.

One method in which these goals can be achieved is by using very fine particles in the sub-micron region. In order to achieve a uniformly consolidated compact it is advantageous to use a well-dispersed colloidal slurry which contains more than 50 volume % solids while still maintaining relatively low viscosities (generally, a viscosity below 100 Pa.s is indicative of a flowable slurry) [1]. This enables the ceramic body to be formed into complex geometric shapes with a defect-free microstructure after sintering.

CHAPTER 2 LITERATURE REVIEW

2.1 Overview

This chapter will introduce the fundamentals of colloid science and surface chemistry with a specific view for ceramic processing. In the section relative to colloidal science we try to understand the science behind behaviour of ceramic powder particles that have dimensions, in the range of 1nm to 1 μ m. These particles are considered colloids and have the tendency to stick to each other. In ceramic processing the surface forces that cause sticking have to be controlled. In order to produce a slurry with desirable properties, a number of suspension parameters must be carefully considered. Stability is the most desired property in a ceramic suspension.

Furthermore, this chapter will give some fundamental theories on forming techniques, with a section on casting techniques that can be broadly classified as direct consolidation methods using gelcasting, Colloidal based consolidation methods, and Consolidation methods using evaporation.

The last section will be focussed on to the sintering, since the fabrication of ceramics commonly includes a heat treatment step in which a powder, already formed into a required shape, is converted into a dense solid.

2.2 Science of Colloidal Processing

2.2.1 General

One of the most promising strategies for producing high-quality ceramics from powders is the wet-processing route. Fewer and smaller defects can be expected in the final microstructure due to better control of particle-particle interactions and increased homogeneity of particle packing in the wet stage compared to dry processing. Many attempts have been made in recent years to improve ceramic processing by new forming techniques. This can be achieved by either consolidating the dispersing medium or by coagulating the suspended particles.

Consolidation of the dispersing medium is applied in gelcasting [2-4] where monomers in the suspension are polymerized or polymer gelation is induced at higher temperature [5]. Polymerization or gelation can be induced by UV radiation [6], by heat [7], or by a means of a catalyst [3].

In flocculation and coagulation of a densely packed suspension, the interparticle forces are controlled in order to accomplish a liquid-to-solid transition. Consolidation may be induced either by applying heat, changing pH, or by increasing the ionic strength of the suspension. Bergström [8] and Napper [9] used a sterically stabilized suspension and destabilized it by heating to form a rigid green body. Lange [10], Velamakanni and coworkers [11,12] and Franks et al. [13] coagulate suspensions by adding salt and then increase the solids loading by pressure filtration or centrifugation. Pujar et al. [14] proposed a reaction injection molding method using heterocoagulation of silica-alumina mixtures.

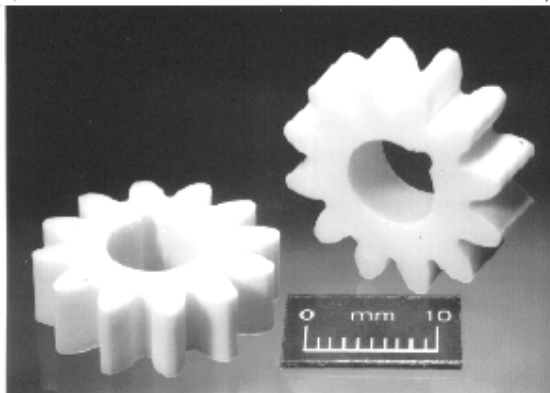
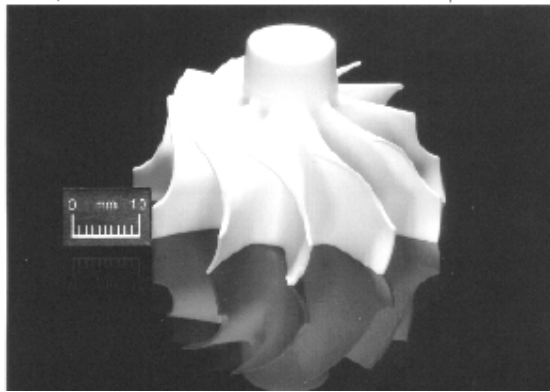


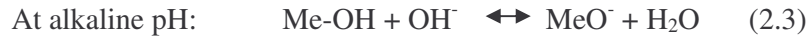
Fig. 2.1: Complex parts made by gelcasting. From top, an alumina turbocharger rotor, and a silicon nitride turbine wheel.

2.2.2 Basics

In water, metal oxide surfaces are hydrolyzed:



Depending on the pH of the liquid, the neutral particle surface will react further, forming either positive or negative surface charges [18]:



When no absorbing compounds are present, the pH therefore controls the surface charge and the surface potential Ψ_0 . The pH at which the net surface charge of the suspended material is zero is called the isoelectric point (IEP). It is not a characteristic of the pure compound alone, but depends on the suspension properties as well-it can, for instance, be shifted by the presence of adsorbants that change the chemical nature of the particle surface.

According to DLVO theory[19], the net force between particles in an electrostatically stabilized suspension is the sum of the attractive Van der Waals forces and the electrostatic repulsion caused by the double layer of ions around the particle.

Depending on the nature of two contradicting forces, the resulting potential curve can show a high energy barrier preventing the particles from touching (stabilized suspension) or a barrier low enough to allow the particles to reach the primary minimum (coagulation). Furthermore, secondary minima can exist, mostly shallow ones that lead to weakly attractive forces. The double layer responsible for the electrostatic repulsion consists of the rather tightly bound Stern layer of counterions and the diffuse double layer in which counterions and co-ions diffuse freely.

Within the Stern layer, the potential Ψ (V) drops linearly from Ψ_O to Ψ_S . In the diffuse double layer, the potential decreases approximately according to:

$$\Psi = \Psi_S e^{-K(d-d_s)} \quad (2.4)$$

Ψ_S being the Stern potential, d the distance from the particle surface, and d_s the thickness of the Stern layer. K is the reciprocal of the double layer thickness (or Debye-Huckel length), which is defined as the distance from the Helmholtz plane at which Ψ has dropped to $1/e$ of Ψ_S . It is given by

$$1/k = \sqrt{\frac{\epsilon \epsilon_o RT}{F^2 \sum_i c_i z_i^2}} \quad (2.5) [35]$$

Where ϵ_o (A s/V m) is the permittivity of vacuum, ϵ is the dielectric constant of the dispersant liquid, F (C/mol) is Faraday's constant, R (J/Kmol) the gas constant, c_i (mol/l), and z_i (-) are the concentrations and valences of the ions present in the liquid. The latter add up to the ionic strength I (mol/l) of the liquid:

$$I = \frac{1}{2} \sum_i c_i z_i^2 \quad (2.6) [35]$$

The higher the ionic strength, the quicker the potential drops with increasing distance from the particle surface, the thinner therefore the double layer becomes.

In summary, the double-layer repulsion of given particles in an electrostatically stabilized suspension depends on the pH, the kind and concentration of dissolved salts, and the possible presence of adsorbing compounds. For destabilizing the suspension, there are two possibilities: shifting the pH to the IEP (i.e. decreasing the surface potential to zero) and increasing the ionic strength (i.e. shrinkage the double layer, thus reducing the range of the double-layer repulsion).

2.2.3 Surface and interfacial phenomena

Surface and interface phenomena play a particularly important role in ceramics processing because powder systems have a relatively high surface area/mass and the adsorption and distribution of additive phases on the surfaces may alter the microstructure and processing behaviour quite markedly[20].

The relevant interatomic forces can be classified according to their range: Coulombic forces which have a long range, Van der Waals forces which are considered “long ranged” on an atomic scale but are short ranged on a macroscopic scale, and the very-short-ranged forces resulting from the exchange or nonexchange of electrons (covalent bonding, hydrogen bonding, and Born repulsions). When all the interatomic forces are summed, they are very-short-ranged and contribute only to the interaction of atoms with their immediate neighbors. Thus it is only atoms at the surfaces or interfaces between materials that contribute to these forces, although, as we shall see below, their effect can sometimes propagate for several atomic or molecular diameters in a liquid. The Van der Waals interactions decrease with the inverse seventh power of distance between atoms; summing over all the atoms in a body increases this range significantly, to the inverse third or second power depending on the geometry of the bodies. But it is still the closest atoms which dominate the summation, i.e., those nearest to the surfaces of the bodies, and the resulting force is a function of the surface separation. Long-ranged coulombic interactions arise between charges, which most often reside at the surfaces of the bodies. Later we will encounter other contributions, such as capillary and salvation effects, arising from the nature of the medium between the bodies and its interaction with the surfaces. Forces due to these effects depend on the thickness of the medium. Thus, all of these contributions to the force between two bodies depend not on the distance between the centers of the bodies but the distance between their surfaces, hence the name surface forces.

2.2.4 Electrical double layer

For electrostatically stabilized colloidal suspensions, the charges, as we have seen, consist of a surface charge on the particles and an equal and opposite countercharge in the solution. Suppose a particle has a positive surface charge due to preferential adsorption of positive ions. In the complete absence of thermal motion an equal number of negative ions (counterions) would adsorb onto the positive charge and neutralize it. However, such a compact double layer does not form because of thermal motion. Instead, the counterions are spread out in the liquid to form an diffuse double layer as shown in Fig. 2.2. There is a fairly rapid change in the concentration of the positive and negative ions as we move away from the surface (Fig.4.10a). As a result, the electrical potential also falls off rapidly with distance from the surface (Fig. 4.10b).

As two particles approach one another in the liquid, the diffuse double layers will start to overlap. It is the interaction between the double layers that gives rise to the repulsion between the particles. If the repulsion is strong enough, it can overcome the Van der Waals attractive force, thereby producing a stable colloidal suspension.

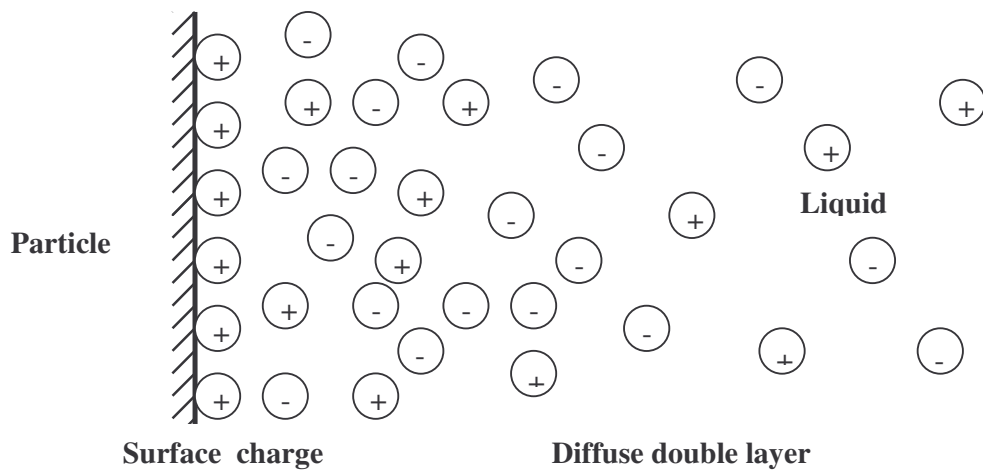


Fig. 2.2: The distribution of positive and negative charges in the electrical double layer associated with a positively charged surface in a liquid.

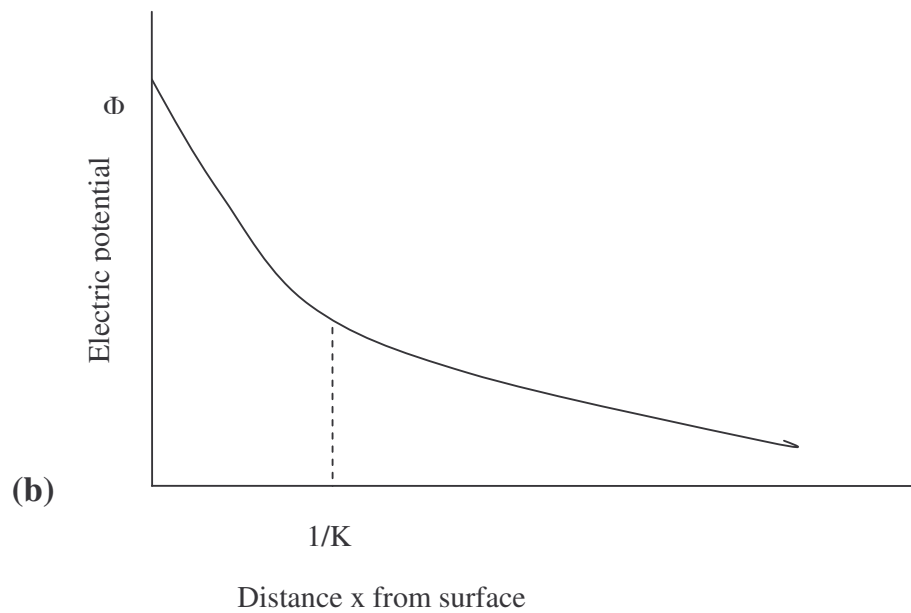
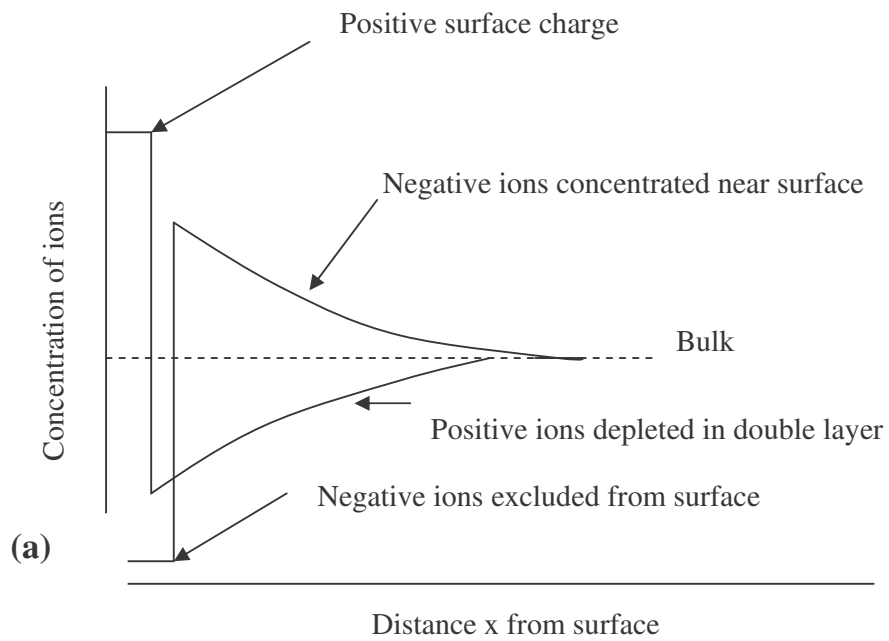


Fig. 2.3: (a) Concentration of positive and negative ions as a function of distance from the particle surface. (b) The electrical potential Φ as a function of distance from the particle surface. The distance equal to $1/K$ is the Debye length.

2.2.5 Significance of the ζ -potential

The ζ -potential determined from the electrophoretic mobility represents the potential at the surface of the electrokinetic unit moving through the solution. It is an indication of the gradient in electrical potential when the surface potential remains constant. It is not the potential at the surface of the particle but must correspond to a surface removed from the particle surface by at least one hydrated radius of the counterion (sometimes referred to as the shear plane).

The ζ -potential plays an important role in that it is widely used as a measure of the stability of colloidal suspensions. The pH at which the zeta potential is zero is termed the isoelectric point IEP. Suspensions prepared at pH values close to the isoelectric point (IEP) may flocculate fairly rapidly because the repulsion may not be sufficient to overcome the Van der Waals attraction. Farther away from the IEP, we should expect the rate of flocculation to be slower. In practice, for good stability, suspensions are often prepared at pH values comparable to those of the plateau regions of the ζ -potential or electrophoretic mobility curve.

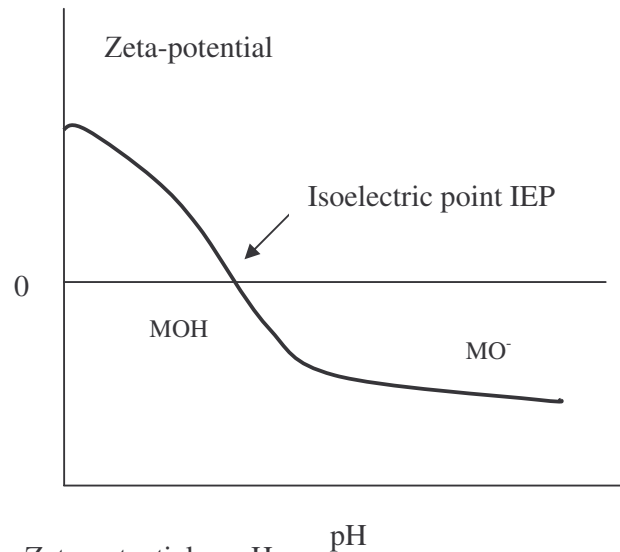
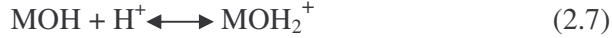


Fig. 2.4: Zeta-potential vs pH

The position of the isoelectric point depend on the dissoziation constants.



2.2.6 Stability of suspensions

Deflocculants and coagulants are essential additives that modify the interparticle forces, agglomerate structure, and consistency of the processing system. Agglomerating forces of the Van der Waals type may be offset by repulsive forces produced by electrical charging and steric hindrance. Particle charging and steric hindrance may produce the deflocculation of particles in polar liquids, whereas steric hindrance produces deflocculation in nonpolar liquids. Defloculants generating particle charging may be either simple or polymer electrolytes; the type and concentration must be controlled in order to control the interparticle repulsion indicated by the zeta potential. The pH relative to the IEP may alter the adsorption of a polyelectrolyte[20]. There are several ways for achieving the repulsion between particles which is sufficiently strong to overcome the attractive force, but the most commonly used are:

1. *Electrostatic stabilization* in which the repulsion between the particles is based on electrostatic charges on the particles
2. *Steric stabilization* in which the repulsion is produced by uncharged polymer chains adsorbed onto to the particle surfaces
3. *Electrosteric stabilization*, consisting of a combinaison of electrostatic and steric repulsion, achieved by the adsorption of charged polymers (polyelectrolytes) on to the particle surfaces

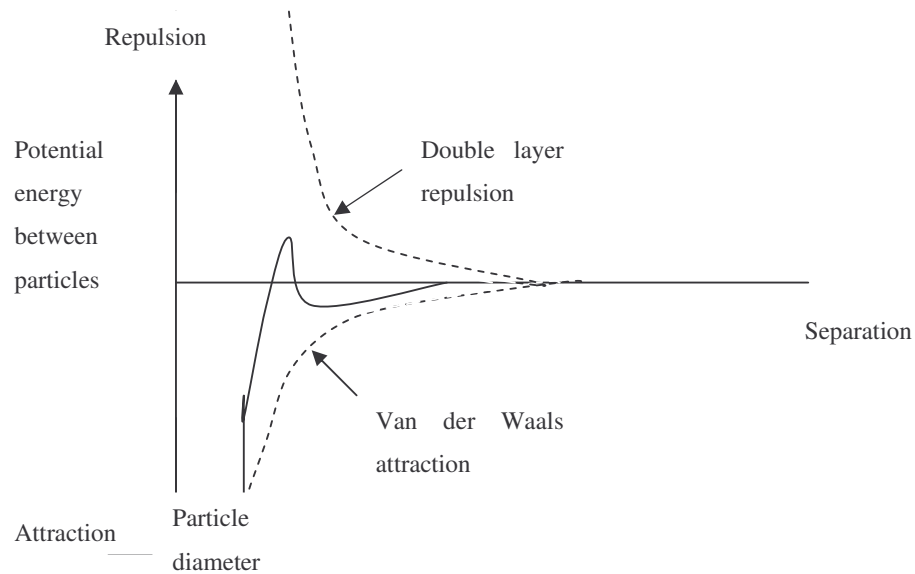


Fig. 2.5: The potential energy between two particles in a liquid resulting from the effects of the Van der Waals attraction and the double layer repulsion[23]

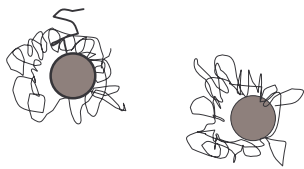
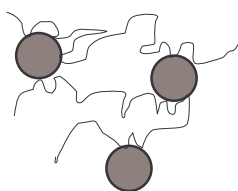
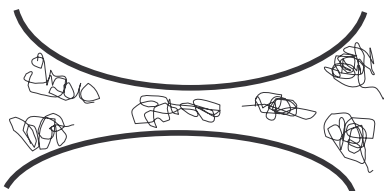
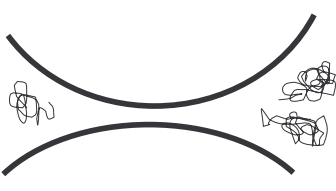
	REPULSION	ATTRACTION
<i>Adsorbing polymer</i>	 Steric stabilization	 Bridging flocculation
<i>Nonadsorbing polymer</i>	 Depletion stabilization	 Depletion flocculation

Fig. 2.6: Summary of the most important effects occurring in the stabilization of suspensions with uncharged polymer chains[23].

2.2.7 Dissociation of Polyelectrolytes in solution

In aqueous solvents, polymers with ionisable groups develop electrostatic charges by dissociation. The dissociation of the polymers as well as their adsorption is strongly influenced by the properties of the solvent and the particle surfaces. Figure 2.7 shows schematically the structure of a common homopolymers used for electrosteric stabilization: poly(acrylic acid) (PAA) having a carboxylic acid (COOH) functional group. The ammonium salt of this polymer, where the H in the COOH group is replaced by NH_4 , is also commonly used in electrosteric stabilization. This polymer is an example of anionic polyelectrolyte in that it dissociates to give negatively charged species.

The functional group of PAA can exist as COOH or dissociated to COO^- . The dissociation reaction can be written in a general form as



Depending on the pH and the ionic concentration of the solution, the fraction of the functional groups which is dissociated (i.e., COO^-) and which is not dissociated (i.e., COOH) will vary.

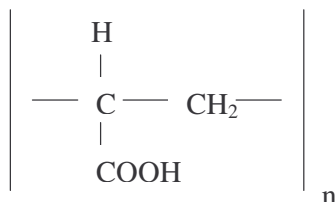


Fig. 2.7: Schematic diagram showing the polymer segments of poly(acrylic acid) (PAA) [23].

2.2.8 Adsorption of Polyelectrolytes from solution

Adsorption of polyelectrolyte onto the particle surface is commonly dominated by electrostatic interactions and is often strongly favored if the particle surface and the polyelectrolyte have opposite charges. The surface charge of the oxide particles dispersed in aqueous solvents depends on the pH of the suspension. Simple ions are adsorbed on oppositely charged surfaces. Complete adsorption of

the simple ions M^+ or A^- can neutralize the surface charge as indicated by the reactions



and

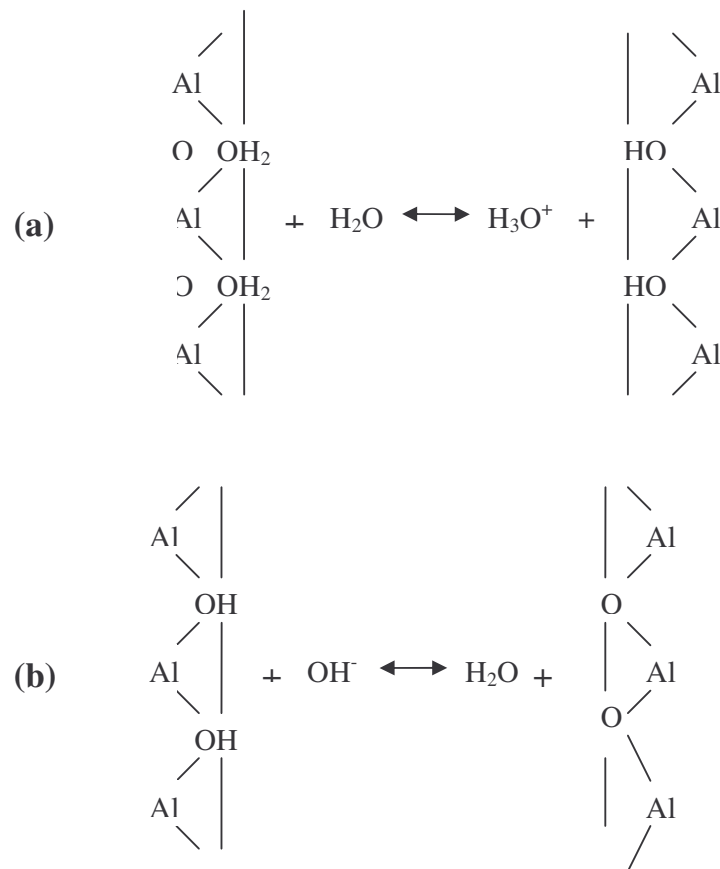


Fig. 2.8: Reaction of the hydrated surface of alumina with (a) an acid and (b) a base [20].

2.3 Rheological Properties of colloidal suspensions

2.3.1 General

The term rheology refers to the deformation and flow characteristics of matter. Rheological measurements monitor changes in flow behaviour in response to an applied stress (or strain). The viscosity of the suspension is the key rheological parameter of interest in ceramic processing, but other parameters such as the yield stress in compression (or shear) and the viscoelastic properties (e.g., storage modulus and the loss modulus) under an oscillatory stress are also important in many systems.

Rheological measurements are widely used to characterize the properties of colloidal suspensions. They can be used as a method of analysis as, for example, the optimum concentration of dispersant required to stabilize a suspension by measuring the viscosity of the suspension as a function of the concentration of dispersant added. Rheological measurements can be used as a direct processing parameter. For example, when the suspension is consolidated by casting methods (e.g., slip or tape casting), it is required, on the one hand, that the suspensions contain the highest possible fraction of particles. This is because a concentrated suspension serves to reduce the shrinkage during drying of the cast and to produce a green body with high packing density. On the other hand, it is also necessary for the suspension to have a low enough viscosity so that it can be cast into the desired shape. Rheological measurements provide an important means of optimizing these requirements[23,24].

2.3.2 Rheological models and properties

1. Newtonian Fluid

The shear stress τ is related to the shear strain rate $\dot{\gamma}$ by

$$\tau = \eta \dot{\gamma} \quad (2.12)$$

where η is the viscosity with η independent of the shear rate (or shear stress).

Many simple liquids (e.g., water, alcohols, and some oils) as well as many molten glasses show Newtonian behaviour[20].

2. Non-Newtonian Fluid

For more complex systems such as polymer solutions and colloidal suspensions, η is not independent of the shear rate

$$\eta(\dot{\gamma}) = \frac{d\tau}{d\dot{\gamma}} \quad (2.13)$$

$\eta(\dot{\gamma})$: viscosity at a given strain rate

When the viscosity decrease with increasing shear rate the behaviour is described as shear thickening (or dilatant).

When the viscosity decrease with increasing shear rate the behaviour is described as shear thinning or pseudoplasticity[20,24].

$$\tau = K \dot{\gamma}^n \quad (2.14)$$

K: consistency index

n: exponent that indicates the deviation from Newtonian behaviour

n=1, the suspension is Newtonian

n<1, the suspension shows shear thinning or pseudo plastic flow

n>1, the flow is described as shear thickening or dilatant.

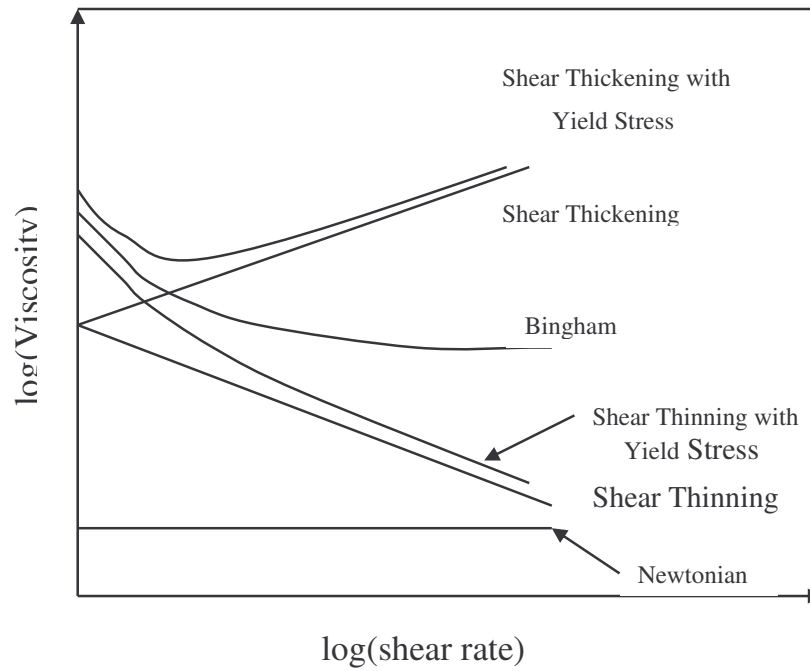


Fig. 2.9: Variation of log (viscosity) with log (shear rate) for the different models of flow behaviour [20].

2.3.3 Factors influencing the rheology of colloidal Suspension

The important factors influencing the rheology of colloidal suspension are:

- ❖ Interparticle forces have a significant influence on the rheological behaviour and the stability of the suspension
- ❖ Particle characteristics, particularly the particle concentration, can also have a significant effect on the suspension rheology.

2.3.3.1 Influence of interparticle force

1. Hard sphere systems:

Hard sphere colloidal systems do not experience interparticle interactions until they come into contact, at which point the interaction is infinitely repulsive. Such systems represent the simplest case, where the flow is affected only by hydrodynamic interactions and Brownian motion. Hard sphere systems are not

often encountered in practice. They serve as a useful starting point for considering the more complicated effects when interparticle forces are present.

2. Soft systems sphere

Colloidal suspensions can be classified as soft sphere systems because the repulsion interactions occur at some characteristic distance from the particle surface. For electrostatic and steric stabilization, this distance is the Debye length ($1/K$) and the thickness of the adsorbed polymer layer, respectively. For sterically stabilized suspensions, the adsorbed polymer layer leads to an increase in the hydrodynamic radius of the particle.

3. Flocculated systems

Flocculated suspensions are dominated by attractive interparticle interactions and form disordered, metastable structures. Because of these nonequilibrium structures, the rheological behaviour is difficult to characterize. It is common to distinguish between two types of flocculated systems which are dependent on the magnitude of the interparticle attraction: weakly flocculated and strongly flocculated.

4. Influence of particle interactions on the viscosity

The interactions between the particles have a dramatic effect on the viscosity of the suspension, as illustrated in Fig. 2.10 for Al_2O_3 suspensions containing 50 vol.% particles which are stabilized with the polyelectrolyte Darvan C. The viscosity decreases dramatically as the concentration of dispersant is increased and, at some critical concentration corresponding to the amount required to form a complete monolayer on particle surface, reaches a low plateau region that is almost independent of the Darvan C concentration. This dramatic change in viscosity reflects the change from a flocculated suspension at low Darvan C concentration to an electrosterically stabilized system above the critical Darvan C concentration. After the critical concentration is reached, further additions of Darvan C serve mainly to produce excess polymer in the solution, and the viscosity of the suspension starts to increase again at high concentration.

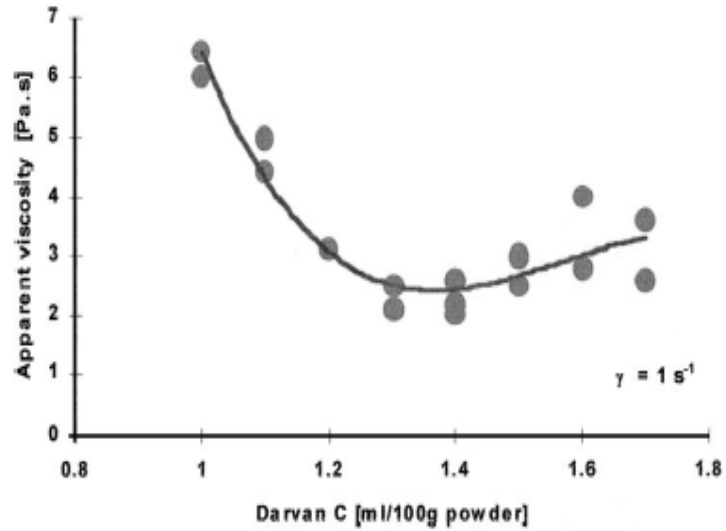


Fig. 2.10: Apparent viscosity of a slip as a function of dispersing agent concentration[24].

2.3.3.2 Influence of particle characteristics

The particle concentration also has a significant effect on the rheological properties of the suspension. At the same level of stability, the viscosity of the suspension increases with increasing volume fraction of particles. The viscosity increases rapidly as the particle concentration approaches f_m (the maximum volume fraction of particles that can be accommodated in the suspension before flow ceases).

The packing of particles can have a significant effect on the rheological properties of a suspension. Several studies have shown how the use of a bimodal or a broad continuous particle size distribution can lower the viscosity and increase f_m , but in many cases, large particles have been used where colloidal effects play no significant role.

The shape of the particles also has an effect on the viscosity. Most advanced ceramics are fabricated using nearly equiaxial particles, but the effect of shape would be important, for example, in the colloidal processing of ceramic composites reinforced with whiskers (short single crystal fibers) or platelets.

2.4 Forming Methods

2.4.1 General

The common ceramic forming methods are summarized in table 2.1

Table 2.1: Aspect of Powder Forming Processes

FORMING METHOD	FEED MATERIAL	MOLD	SHAPE
Dry or semidry pressing			
Die compaction	Powder or free-flowing granules	Metal die, surface relief in punch	Small simple shapes
Isostatic pressing	Powder or fragile granules	Rubber mold, complex/simple shape	Larger, more intricate shapes
Hot pressing		Refractory ceramic/metal die	Dense structural, material stock and shapes
Deformation of a plastic mass			
Extrusion	Moist mixture of powder and binder solution		Elongated shapes with uniform cross section
Injection molding	Granulated mixture of powder and solid binder	Metal die	Small intricate shapes
Casting of a slurry			
Slip casting	Free-flowing slurry with low binder content	Porous gypsum/polymer	Thin intricate shapes
Tape casting	Free-flowing slurry	Metal blade	Thin sheets
<i>Gel casting</i>	Free-flowing slurry with monomer that polymerize to form a binder	Metal/polymer mold	Complex shapes, good powder dispersion, uniform density

2.4.2 Casting Methods :Direct Consolidation Forming Methods

Direct consolidation forming methods can be broadly classified as:

- Direct consolidation methods using gelcasting;
- Colloidal-based consolidation methods; and
- Consolidation methods using evaporation.

In the first category, the generic principle is to encourage polymers (or monomers reacted to form polymers) to create a 3-D network that locks the suspended particles together, thereby preventing particle agglomeration as the article is dried. Gelcasting is a recently introduced process that is based on ideas taken from the traditional ceramics industry and the polymer industry[27,28].

As summarized in Figure 2.5, a slurry of ceramic particles dispersed in a monomer solution is poured into a mold, and the monomer is polymerized to immobilize the particles and to form a gel-like bonding phase (i.e., a binder). The system is removed from the mold while still wet, dried by evaporation of the liquid, heated to burn out the organic additives, and finally sintered.

Gelcasting commonly employs aqueous solvent (although organic solvents can also be used), dispersants, and processing methods (e.g. ball milling) similar to those used in traditional slip casting to produce the commonly desired slurry properties for casting: stability against flocculation, high particle concentration (~50 vol% for gelcasting), and a low viscosity. The key element of the process is the addition to preventing segregation or settling of the particles, the gel provides strength to the body to withstand capillary stress during drying so that thick as well as thin parts can be formed. There is only 2-4 wt% of polymeric material in the dried body, a value that is comparable to the amount of organic additives in die-pressed bodies formed from spray-dried granules and slip-cast bodies, so binder burnout is not normally a limiting step.

Table 2.2: Examples of compositions for gelcasting[23].

CERAMIC POWDER	DISPERSANT	MONOMER SOLUTION	INITIATOR
Al ₂ O ₃	Ammonium polyacrylate	MAM-MBAM or MAM-PEGDMA	APS/TEMED
Si ₃ N ₄	Poly(acrylic acid)	MAM-MBAM or MAM-PEGDMA	APS/TEMED
SiC	Tetramethyl ammonium hydroxide (pH>11)	MAM-MBAM or MAM-PEGDMA	APS/TEMED

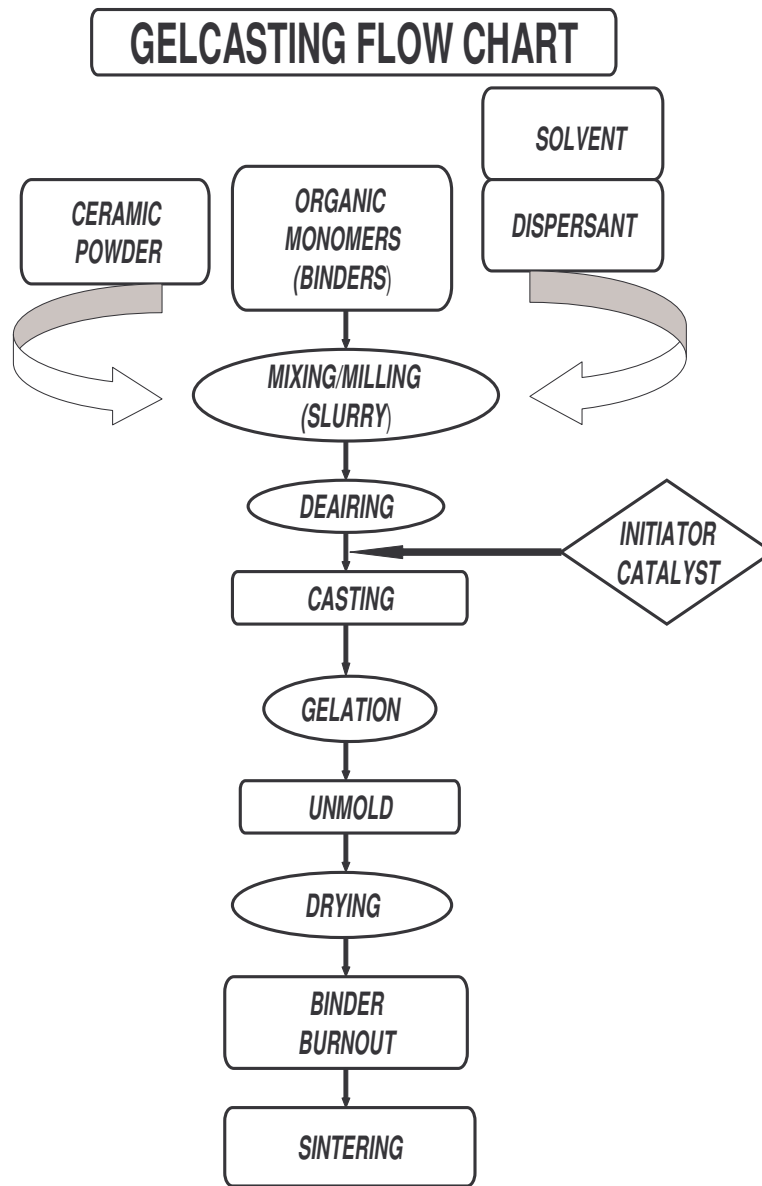


Fig. 2.11: Schematic flow diagram of the gel casting process.

The second main category of direct consolidation techniques is colloid-based techniques, which use the principle of colloid and surface science to consolidate (flocculate) a suspension to obtain sustaining green bodies. Various mechanisms can be used to flocculate a suspension, and, consequently, several methods are available. In direct coagulation casting (DCC) [29,30] and temperature-controlled coagulation casting, a controlled flocculation (coagulation) is achieved by changing the pH of the powders or by increasing the electrolyte concentration.

The last category of direct consolidation techniques, i.e., via evaporation, is successfully used in tape casting. In addition, two interesting binder-free direct consolidation mechanisms recently have been proposed: thixotropic casting and drying induced forming. The main advantage of these two methods is their suitability to produce bulk ceramics having complex shapes.

Thixotropic casting involves vibratory casting of highly thixotropic slurries having high solids loadings such that they become fluid only under vibration[31]. Drying induced forming uses an aqueous slurry that is so extremely concentrated (72 or 91 wt % in the case of alumina) that a minimal evaporation is enough to transform fluid slurry into a self-sustaining body.

2.5 Sintering of Ceramics

2.5.1 General

Because of the high melting point of the raw materials, the fabrication of ceramics commonly includes a heat treatment step in which a powder, already formed into a required shape, is converted into a dense solid. This step is referred to as sintering (or firing). In general, a ceramist, wishing to produce a material with particular properties, must identify the required microstructure and then design processing conditions that will produce this required microstructure. The objective of sintering studies is therefore commonly to understand how the processing variables such as temperature, particle size, applied pressure, particle packing, composition and sintering atmosphere influence the microstructure that is produced [24,32].

2.5.2 Sintering of alumina

In this section a brief introduction is given to the known kinetic factors and mechanisms of sintering including the use of ultrafine transitional alumina powders and the control of their phase transformation into alpha alumina.

2.5.2.1 Alpha-alumina

For engineering ceramics the most widely used material is alpha alumina. However the size of commercially available powders is typically above 200 nanometers and require relatively high sintering temperatures. The sintering of alpha alumina ceramics is affected by a number of factors, the most relevant being the maximum sintering temperature, sintering time, the mean grain size, the maximum sintering pressure and the type and amount of sintering additives. These factors are usually addressed during the investigation of sintering mechanisms. For further optimisation of the sintering process, other aspects which have a significant impact have to be taken into consideration. These are the

sintering atmosphere, the grain size distribution, the powder processing techniques, and the sintering profile.

Commercially available alpha alumina (corundum) is a rather coarse material with a fairly low reactivity and virtually no reaction with water in the bulk. However, ultrafine grained highly reactive alpha alumina has been produced hydrothermally from very fine alumina under 10 – 100 bar vapour pressure at temperatures ranging from 320 °C to 400 °C. Typically particle sizes between 30 and 80 nanometers with apparent density of 3.7 g/cm³ compared to 3.98 g/cm³ for single crystalline corundum have been reported[33]. Sintering involves the densification of a powder compact to remove pores and develop sufficient strength at grain boundaries between particles. This required material transport into pore volume. Alpha alumina is reported to densify by solid state sintering, and three stages can be considered.

a. Initial stage of sintering

Particle rearrangement takes place and more efficient particle packing is achieved, which occurs under the impact of pressure or the presence of a liquid phase formed during heating.

b. Intermediate stage of sintering

During the intermediate stage of sintering open pore channels close up with only a little grain growth occurring. The densification rate is relatively fast at this stage.

c. Final stage of sintering

During the final stages the closed pores are removed. Densification becomes slow, while significant grain growth takes place which retards densification. The control of grain growth is important to fully densify a powder compact.

The driving forces for sintering are primarily the reduction of free surface area (surface-pore interface), or the transformation of high energy surface area into lower energy grain boundary area. The grain boundary areas are reduced on increasing even lower energy bulk volume, that is, increasing the grain size with more atoms located in a three dimensional lattice environment.

Constructive mechanisms contributing to densification are volume diffusion in which the atoms diffuse through the bulk of the grain towards the interface region where a neck is formed. This extends the grain boundary area and grain boundary diffusion is increased along this neck region, and material simultaneously diffuses and extends. Centre-to-centre approach of the grains is observed, with material

transport into the pores occurring by increasing the neck region. By applying pressure (hot isostatic pressing HIPing), creep mechanisms may also contribute.

The sintering theories consider mean particle size, temperature, pressure and diffusion constants as the main parameters governing densification. Though all the mechanisms are active at the same time, one usually dominates and is sufficient to describe the sintering process at this stage. It may happen that mechanisms change as the densification proceeds. Both oxide additives and optimised processing can reduce sintering temperatures to full density well below 1500 °C – 1600 °C.

While the effects of particle size, temperature and pressure can be modelled quite well and trends can be predicted, the aspects of pore size distribution and porosity, degree of particle agglomeration, homogeneity and purity describe the real world of ceramic sintering. The effects of improving on processing steps have been demonstrated by Krell et al, 1995 who prepared green compacts of an ultrapure fine alpha alumina (Taimicron TM-DA with a mean particle size of 0.2 microns) by a number of methods with the aim of minimising the sintered grain size. The results of the hardness measurements are shown in Table 2.3. Starting from a basic approach with attrition milling, freeze drying and uniaxial pressing, a sintering temperature of 1450 °C at normal pressure was required to achieve compacts with 98-99 % relative density and grain sizes of 1.25 micrometers. Changing to pressure filtration with appropriate dispersion of the powder and subsequent cold isostatic pressing led to drastic temperature reductions of 100 °C with grain size reductions of 2/3 and a hardness increase from HV (10) = 17 to 22.5 GPa.

Table 2.3: Vickers hardness (GPa) of Alumina Ceramics[45]

MATERIAL	MICROHARDNESS (LOAD<5N)	MICROHARDNESS (LOAD>100N)
Single crystal (sapphire)	23-27 GPa	14-17 GPa
Sintered alumina		
Grain size ~2 μ m, relative density > 99%	20 – 26 GPa	16.5 – 18.5 GPa
Grain size ~0.2–0.45 μ m, relative density ~ 98-98.5 %	19 – 25 GPa	19 – 20 GPa

While Krell and Blank, 1995 concentrated on refining the final grain size in the matrix, Yeh and Sacks, 1988 focused on reducing the sintering temperature of alpha alumina powder (Sumitomo AKP-50 powder, 0.2 micrometers). Yeh et al, 1988 utilised particle refinement, electrostatic dispersion of the alumina powder and slip casting to achieve high green densities. The starting powder was refined by centrifugal sedimentation resulting in a particle size distribution of 0.07 to 0.1 micrometers with a specific surface area of 23.8 m²/g. The powder was dispersed and stabilised by adjusting the pH to 4 in an aqueous suspension which resulted in a castable slurry with a solids content of 25 volume %. Using conventional slip casting, a green compact density of 69 volume% was obtained, with a fairly narrow pore size distribution of around 10 nanometers. After drying, the compact was pressureless sintered at 1150° C.

Roosen et al, 1988 studied the green density as a function of pore diameter and processing methods and according to their findings, a relative green density of 55% was measured for a particle size of around 100 nanometers. It was further established that within a certain range there is a correlation between the mean pore size in the green compact and the temperature of maximum shrinkage.

2.5.2.2 Transitional alumina powders

Commercial alumina powders smaller than approximately 150 nanometers are typically of metastable modification. The alumina powders used in ceramic processing range from hydroxides such as $\text{Al}(\text{OH})_3$, AlOOH (Boehmite) to oxides. The oxide modifications are shown in Figure 2.12. Typically, boehmite and gamma alumina can be produced with extremely fine grain sizes reaching below 10 nanometers and resulting in a very high surface reactivity. All these oxides are sometimes collectively referred to as gamma-alumina.

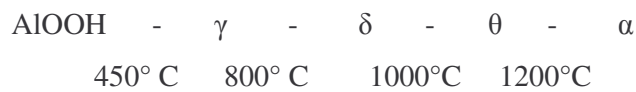


Fig. 2.12: Alumina phase relationships[32]

2.5.2.2.1 Gamma-alumina

Gamma alumina crystallises in a cubic structure which is analogous to the spinel structure, compared to alpha alumina which is hexagonal. About 3.4 – 3.8 wt.% water can be accommodated in the lattice which disappears when heated at temperatures between 600 °C and 800°C. The density of gamma alumina is reported to be approximately 3.50 g/cm³.

The control of the phase transformation from, delta or theta (γ , δ , θ) to alpha (α) is crucial during the sintering period. Pure gamma alumina transforms into alpha at temperatures between 1250°C and 1350°C producing a coarse vermicular grain structure. During sintering the particles of the dense green body formed from filter pressing shrink away from each other leading to a coarse structure. Furthermore, the phase transformation is slow, leading to preferential grain growth [34,35].

The gamma to alpha phase transformation is a reconstructive solid state reaction with the nucleation step being rate limiting. As soon as an alpha nucleus is

formed it grows rapidly through the untransformed matrix and growth is effectively only slowed down when other alpha grains are impinged. The

specific surface area of the ultrafine gamma powder shrinks to only a few m^2/g which means that an essential loss of driving force which could be utilised in subsequent sintering has occurred.

There are two possible methods to facilitate sintering at low temperatures. To enhance nucleation of fine alpha particles to preserve the specific surface area, and to control the diffusion kinetics so that the phase transformation and densification take place over a drastically reduced temperature span.

CHAPTER 3 EXPERIMENTAL PROCEDURES

3.1 Materials Used

The alumina used in this study was ultrapure submicron alpha alumina AKP-50 with particle size 0.1-0.3 μm , surface area 9-15 m^2/g , was supplied by Sumitomo.

The cBN powder with $d_{90} = 3.21$ used was supplied by Element Six.

The dispersant ammonium poly (acrylic acid) was source from Sigma-Aldrich. The monomer 2-hydroxyethyl methacrylate (HEMA) produced by Sigma-Aldrich was used as gel former. Polyvinyl pyrrolidone (PVP) with an average molecular weight of 40 000 was provided by Sigma-Aldrich. The cross-linker N,N-methylenebisacrylamide (MBAM), the catalyst N,N,N',N'-tetramethylethylenediamine (TEMED), and the initiator Ammonium persulphate $(\text{NH}_4)_2\text{S}_2\text{O}_8$ were produced by Sigma-Aldrich.

Table 3.1: Materials used

Material Used	Supplier	Mean Particle Size (μm)	Surface Area (m^2/g)	Phases present	Particulars
AKP-50 alumina	Sumitomo	0.1~0.3	9~15	Alpha	High purity 99.99%
cBN	Element Six	4.5~5	1~1.60	Cubic	High purity
Defocculant: Ammonium poly (acrylic acid)	Sigma-Aldrich			Polyelectrolytes	High purity
Monomer: 2-hydroxyethyl methacrylate (HEMA)	Sigma-Aldrich			Monomer	High purity $\geq 97\%$
Cross-linker: N,N-methylenebisacrylamide (MBAM)	Sigma-Aldrich			Monomer	High purity $\geq 99\%$
Catalyst: N,N,N',N'-tetramethylethylenediamine (TEMED)					High purity $\geq 97\%$
Initiator: Ammonium persulphate $(\text{NH}_4)_2\text{S}_2\text{O}_8$					High purity $\geq 99\%$
Antifoam: Silicone oil Tributylphosphate n-octanol	Merck				High purity $\geq 99\%$
Polymer: polyvinyl pyrrolidone (PVP)				Polymer	High purity $\geq 99\%$
Binder: polyvinyl alcohol	Aldrich				High purity $\geq 99\%$
Plasticizer: polyethylene glycol	Aldrich				High purity $\geq 99\%$

3.2 Powder Characterization

3.2.1 X-Ray Diffraction

The analytical technique which was used to characterize the ceramic powders was X-Ray Diffraction (XRD). X-ray diffractograms were measured using a Philips Diffractometer. The phase purity was determined by X-ray diffraction, using a Philips X-ray machine equipped with a PW1830 diffractometer with CuK α irradiation operated at 40kV and 20mA. All measurements were taken using a step scan of 0.020⁰ recorded in the 2 θ regime of 10-80⁰ for 1hour 30minutes. Patterns were collected with the aid of APD powder diffraction software and phase identification was done using X'Pert HighScore software containing ICDD (International Centre for Diffraction Data) data files for comparison.

3.2.2 Particle size Distribution

The instrument used for particle size analysis was the Mastersizer2000 Malvern which measures particles in the region 0.01 μ m to 3 mm using the light scattering behaviour of the material. Sample preparation required making up a suspension of the alumina powder in distilled water and dispersing it with a dispersant Ammonium polyacrylic acid and ultrasonic treatment. 1g powder was dispersed in 10 ml distilled water, and 2 ml of this solution was then dispersed in 1000 ml distilled water and particle size measurement was performed. A software performed three measurements and gave the average of the figures measured as a result.

3.2.3 Specific Surface Area

The BET technique makes use of pressure/volume measurements to determine the amount of adsorbate gas before and after exposure to the adsorbent. As adsorption or desorption occur the pressure in the sample cell changes until equilibrium pressure is the difference between the amount of gas admitted or removed and the amount required to fill the space around the adsorbent.

The specific area of all powders was determined by nitrogen adsorption using the multipoint BET method on the Quantachrome Autosorb-1.

3.3 Slurry preparation

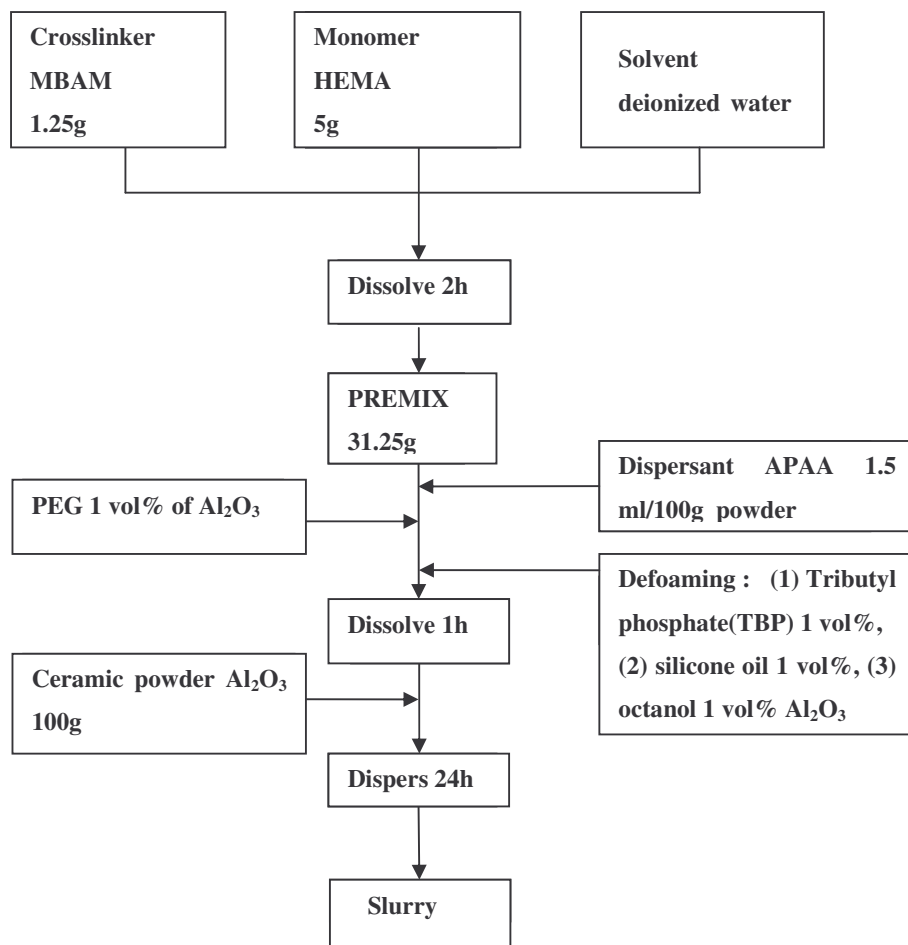


Fig. 3.1a: Slurry preparation for gelcasting process with HEMA is summarized in the flow sheets above, together with the materials used throughout the study.

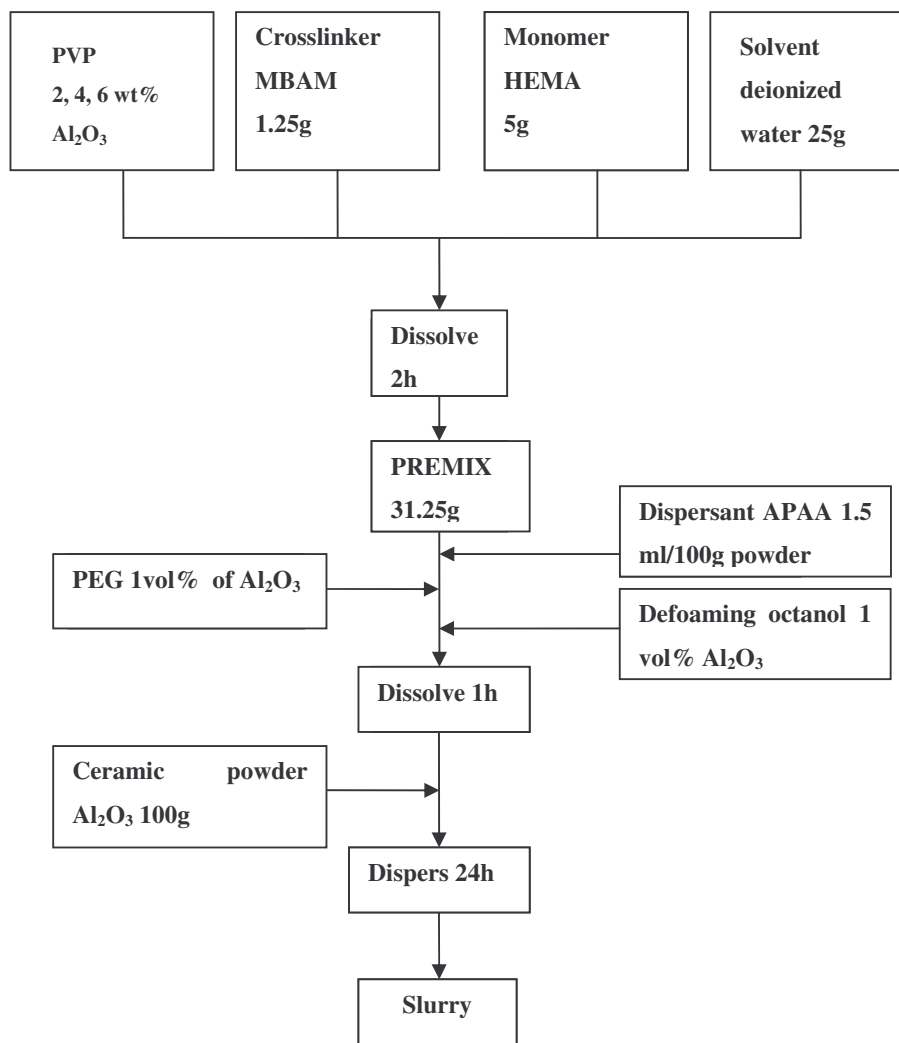


Fig. 3.1b: Slurry preparation for gelcasting process with HEMA-PVP system is summarized in the flow sheets above, together with the materials used throughout the study.

The flow chart of the present gelcasting process is shown in Fig. 3.1a. In first step a premix of monomers dissolved in water is prepared. Hydrogel formulation : hydroxymethacrylamide (MAM) is used as the main monomer and N,N',-methylenebisacrylamide (MBAM) is used as the cross-linker and both are mixed and dissolved in deionized water for 2 hours . In the second step a suitable dispersing agent (ammonium poly acrylic acid), a plasticizer (polyethylene glycol) and a defoaming agent(three different defoaming agents were tested:(1) tributyl phosphate, (2) silicone oil, (3) n-octanol) are added to the premix and dissolved for 1 hour. Slurry: the last step involves the preparation of a highly loaded suspension by adding ceramic powder(alumina sumitomo AKP-50). After the mixture is mixed for 24 hours in the ball mill. The pH of the slurry thus prepared was about 8.3

3.4 Rheological Measurement

The rheological properties of the slurry were measured by an advanced Physica MCR300 rheometer (Anton Paar Corp., Ostfildern, Germany) with a concentric cylinder (CC27) with a gap between the inner and outer cylinder walls of 1.33 mm. This is a computer controlled rheometer system with Rheoplus software. This instrument was used to measure the rheological properties of liquid or paste-like materials. The measuring cup used was a concentric geometry which required a sample volume of 22 ml.

The measuring cup was filled with 22 ml of sample and the measuring cell is inserted into the cup. Using the measuring profile flow curve/with pre-shear the sample was presheared for 3 min to ensure thorough blending of ingredients, and held for 3 min before each measurement. The viscosity was monitored over the entire shear rate range between 0 and 1000 S^{-1} .

3.5 Zeta Potential

The Malvern Zeta-sizer 4 was used to determine the zeta potential of the slurries. Experiments carried out were aimed at studying the way in which zeta potential changes with solution pH, electrolyte concentration and the nature of the polymeric surfactant added.

Sample preparation for zeta potential measurements required a stable suspension in aqueous/ polar media. Prior to measurement the instrument was calibrated using a latex standard. Sample preparation involved making up a suspension of the powder in distilled water and dispersing with a dispersant and ultrasonic treatment. 1g powder was dispersed in 10 ml distilled water, and 2 ml of this solution was then dispersed in 1000 ml distilled water and zetapotential measurements were performed. The pH was controlled by adding poly(acrylic acid) or ammonium hydroxide to the suspension prior to measurement.

3.6 De-airing

Deairing is an essential step in gelcasting if high quality, defect free parts are to be obtained. There are three types of bubbles that can form during deairing. These include mechanically entrained air, dissolved air, and boiling solvent. In most gelcasting applications it is critical to remove both the entrained air, which was entrapped during mixing, and also the air dissolved in the solvent phase. Both of these can lead to the formation of strength limiting defects in the gelled part. Bubbles that form from solvent boiling will collapse when the vacuum is released.

Deairing was performed under a vacuum of about 0.03 atm. The slurry contained in 50 ml beaker was placed in a dessicator connected to a vacuum pump. The dessicator was placed in an environmental chamber and maintain at a temperature below 10°C and 90%RH to prevent the drying of the slurry while deairing under vacuum resulting in the formation of flakes of dried material, which can act as flaws in the part. This process was done under the following conditions:

- 1) without defoaming agent added to aid deairing

2) with defoaming agent added to aid deairing. Three different defoaming agents were used:

- Tributyl phosphate
- Silicone oil
- n-octanol

The duration of this operation was 10 minutes. Additional deairing was needed after the addition of the initiator and catalyst.

3.7 Casting Condition and Gelation reaction

Prior to casting, initiator and catalyst were added to the suspension. A 5 wt.% aqueous solution of ammonium persulphate (APS) was used here as initiator. N,N,N,N-tetramethylethylenediamine (TEMED) was used as a catalyst. After intimate mixing with a magnetic stirrer, the suspension undergoes de-airing for 5 min before gelation takes place. The slurry was then cast in cylindrical PVC moulds and gelled ~5min after casting. This allows to retain a reasonable amount of time (10 min) at ambient temperature after the addition of the initiator and catalyst to the slurry for deairing and mold filling. This prevents premature gelation, which destroys the usefulness of the slurry.

3.8 Drying

In the gelcasting process the part is formed without elimination of the liquid phase of the slurry that upon reaction becomes a polymeric gel. In other words, the wet gelcast body contains the same amount of water as the starting slurry. This water has to be eliminated by a subsequent drying step which constitutes the most critical and rate controlling part of the process. After gelation is complete (60 min) the gelled body was removed from the mould. To avoid any differential drying, drying has to be carried out under well-controlled temperature and humidity conditions. The green gelcast body was dried first under high humidity =90%RH and at 40°C in environmental chamber to remove 40-50% of water content. From there on the humidity was lowered to 30%RH and the temperature raised to 90°C to speed up drying.

3.9 Thermal gravimetric analyser (TGA)

Thermo gravimetric analysis was used to determine the range of temperature at which the organic additives are removed. This was achieved by monitoring the %weight change with increasing temperature up to 800°C. This was done on a Perkin Elmer TGA 1 using Pt sample cups under constant gas flows. A platinum rhodium thermocouple situated close to the sample was used for temperature readings. The equipment is coupled with a PC with suitable software for data analyses and storage.

3.10 Binder burn out and presintering

After drying, the parts were further processed in the conventional way. The organic binder (HEMA-MBAM) content is only approximately 5 wt% of the alumina powder. The binder was removed in a separate step or carried out immediately in the sintering furnace. The debinding profile applied was:

Room temperature to 100°C at 10°C/min,
100°C to 400°C at 0.5°C/min,
400°C to 900°C at 5°C/min, dwell at 900°C for 60 min,
900°C to 25°C at 10°C/min.

3.11 Sintering

The Box furnace used for sintering the Al₂O₃ gelcast part was an Elite Furnace supplied by Elite Thermal Systems (Ltd) with silicone carbide heating elements which is capable of operating at temperatures up to 1600°C.

The Sintering atmosphere was air. The sintering profile used was:

Room temperature to 100°C at 10°C/min,
100°C to 400°C at 0.5°C/min,
400°C to 600°C at 5°C/min,
600°C to 1450°C at 10°C/min, dwell at 1450°C for 180 min,
1450°C to 25°C at 10°C/min

Sintering in tube furnace

A horizontal type tube furnace was used for firing the gelcast composite (Al_2O_3 -cBN). This consists of molybdenum disilicide heating elements suspended from the roof to hang freely along the side walls. Insulation was provided for by high temperature refractory board surrounding the tube. A platinum-rhodium thermocouple positioned in the heating chamber was used as a temperature sensor providing raw data for temperature readings to the programmer. A silica type tube 1200mm in length and 40mm external diameter was used as the chamber containment for the flowing gas and sample. The samples were placed in alumina boats in the vicinity of the hot zone (middle section of the chamber). The heating and cooling cycles were programmed through the temperature programmer installed on the furnace. The sintering profile used for Al_2O_3 -cBN was the same with the one used with pure Al_2O_3 .

3.12 Density Measurement

The densities of green and sintered compacts were determined by Archimedes principle.

Archimedes' method for density determination:

- i) Specimen cleaned using isopropanol followed by drying in air at 80°C for 10 minutes. The dry weight of sample W_1 was determined using a balance with an accuracy of 0.1 mg (used for all the weight measurements).
- ii) Specimen was boiled in distilled water for 3 hours.
- iii) The suspended weight of the specimen (W_2) was determined.
- iv) The surface moisture was removed by a light wipe with a damp cloth and the wet weight (W_3) determined.
- v) The procedure was repeated to check consistency of weighing.

The open porosity and bulk densities were determined using the calculations below;

$$\text{True volume of the specimen} = \frac{W_1 - W_2}{\rho_w} \quad (3.1)$$

$$\text{True density of the specimen} = \frac{W_1 \rho_w}{W_1 - W_2} \quad (3.2)$$

$$\text{Volume of open porosity} = \frac{W_3 - W_1}{\rho_w} \quad (3.3)$$

$$\text{Bulk volume} = \text{volume of specimen} + \text{open porosity} = \frac{W_3 - W_2}{\rho_w} \quad (3.4)$$

$$\text{Bulk density} = \frac{W_1 \rho_w}{W_3 - W_2} \quad (3.5)$$

$$\text{Volume fraction of open porosity} = \frac{W_3 - W_1}{W_3 - W_2} \quad (3.6)$$

ρ_w denote the density of water in all cases.

For the green density measurement, the sample was first presintered at 900°C for 1 h before measurement by Archimedes' method.

3.13 Pore size measurement

Pore size were measured by porosimetry for each green body, using the Quantachrome Poremaster – 33/60, Quantachrome Corporation. The Poremaster-60 is designed to measure pore volume for pores with diameters in the range of about 1000 to 0.0035 μm (35 Å) and the Poremaster-33 covers a range from about 1000 to 0.0070 μm (70 Å) pore diameter. For measurement of volumes of pores larger than 7 μm the dual, low pressure measuring and filling station is used.

These stations are used to fill the sample cells with mercury and measure pore volumes in the range of about 1000 to 4.3 μm diameter.

3.14 Grinding and Polishing

A preparation method is a series of steps, in which material is removed mechanically from the sample surface by means of successively finer abrasives. A preparation method usually consists of the following steps:

Plane Grinding, PG

Fine Grinding, FG

Diamond Polishing, DP

Grinding

Grinding removes damaged or deformation surface material, while introducing only limited amounts of new deformation. The aim is a plane surface with minimal damage that can be removed easily during polishing in the shortest possible time. To determine whether a surface is sufficiently flat and free of irregularities one should look for defects on a dry surface. An even pressure was applied to the sample while grinding to keep the surface flat. The sample was moved counter clockwise against the flow of the wheel. The automatic polisher (LECO Spectrum System 2000) was used for this purpose.

We have used the diamond grinding discs, starting with the coarse to the fine one.

Diamond grinding discs used: #220, #600, #1200

Polishing

Like grinding, polishing must remove the damage introduced by previous operations. This is achieved with steps of successively finer abrasive particles.

Diamond spray 1 μm (struers) was used as an abrasive to accomplish the fastest material removal and the best possible planeness. Because of its hardness, diamond cuts extremely well through all materials and phases.

Polishing was carried out on polishing cloths DP-plan (Struers). For diamond polishing, a lubricant had to be used (blue). After polishing, the sample was washed with soapy water and cleaned. It was subsequently rinse in distilled water

and blow-dried. Care was take to avoid touching the polished surface of the sample with fingers.

Table 3.2: Metalog Method

Step	Plane Grinding PG	Fine Grinding FG	Diamond Polishing DP
Surface	Diamond disc	Diamond disc	DP-plan
Abrasive	Diamond	Diamond	Diamond suspension (struers)
Grit/grain size	#220, #600	#1200	1 μ m
Lubricant	Water	Water	Blue
[rpm]	300	300	150
Time[min]	Until surface plane	15-30	10-15

CHAPTER 4 RESULTS AND DISCUSSION

This section covers the overall results of the experiments carried out as described in Chapter 3. This encompasses the characteristics of the alumina slurry and alumina-cBN produced, the characteristics of the green gelcast and sintered gelcast samples.

4.1 Powder Characterisation

4.1.1 X-ray diffraction

Samples of alumina AKP-50 and cBN powders were analysed by XRD.

Results of phases present in these powders are presented in Table 4.1 and Figure 4.1 shows a diffractogram of AKP-50 alumina powder sample between 2-theta values of 10 and 80°C for 1 hour 30 minutes.

The x-ray diffractogram in Fig. 4.1 shows one crystalline phase (high narrow peaks). The crystalline phase is alpha alumina. Fig. 4.2 shows one crystalline phase for cBN, the crystalline phase is cubic boron nitride.

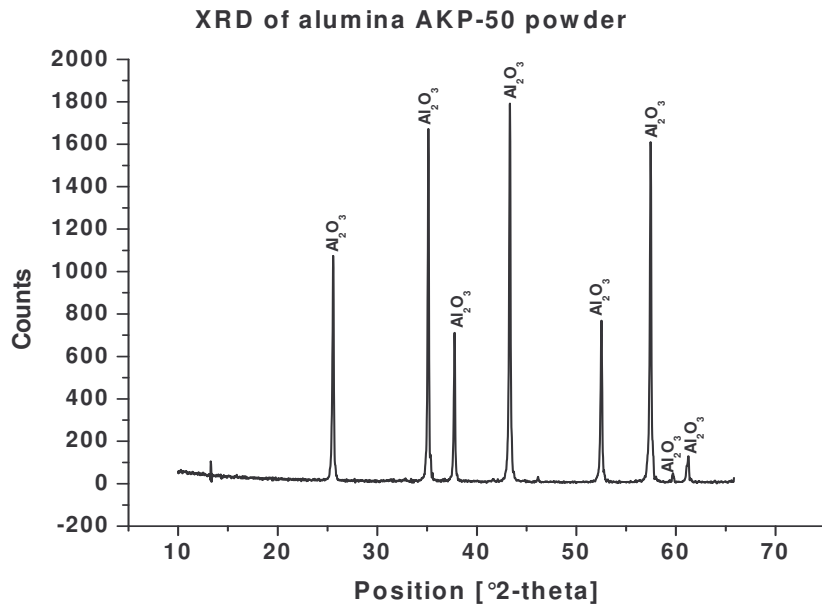


Fig. 4.1: X-ray diffractogram of AKP-50 alumina powder.

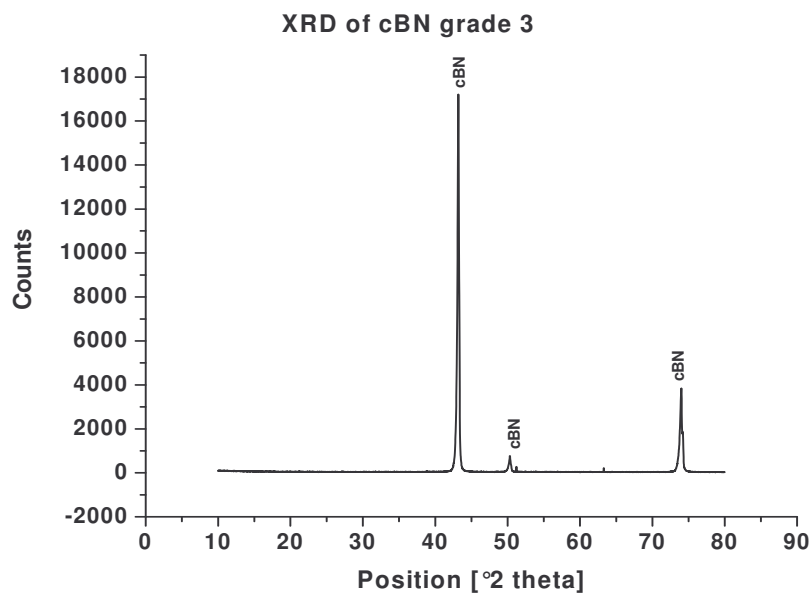


Fig. 4.2: X-ray diffractogram of cBN powder.

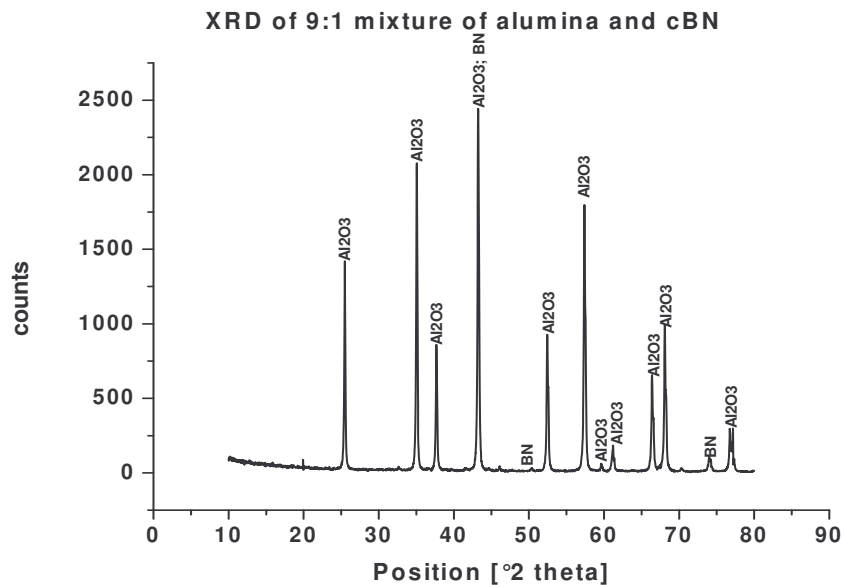


Fig. 4.3: X-ray diffractogram of 9:1 mixture of AKP-50 alumina-cBN powder.

4.1.2 Particle size analysis

Particle sizes of alumina AKP-50 particles were found to be in the submicron range (0.1-0.3 μm) as shown in Figure 4.4. Figure 4.5 shows the mean particle size of 3.2 μm for cBN. The measured particles sizes were in agreement with those determined by the suppliers.

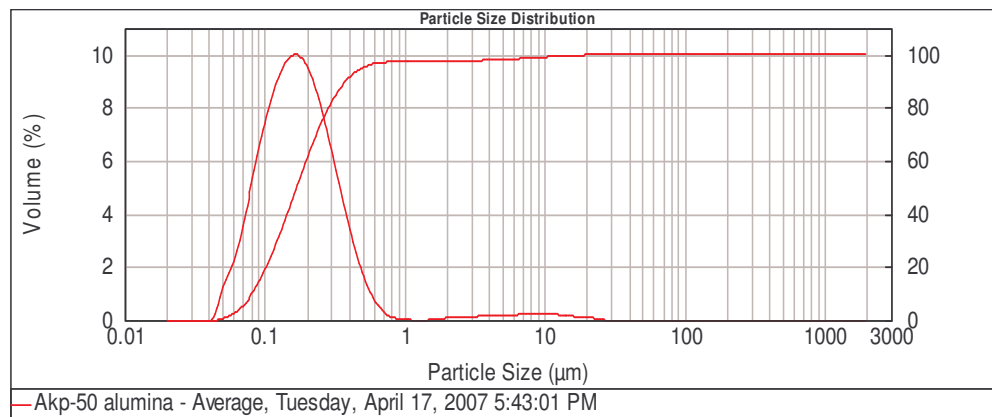


Fig. 4.4: Particle size distribution of raw powder alumina AKP-50.

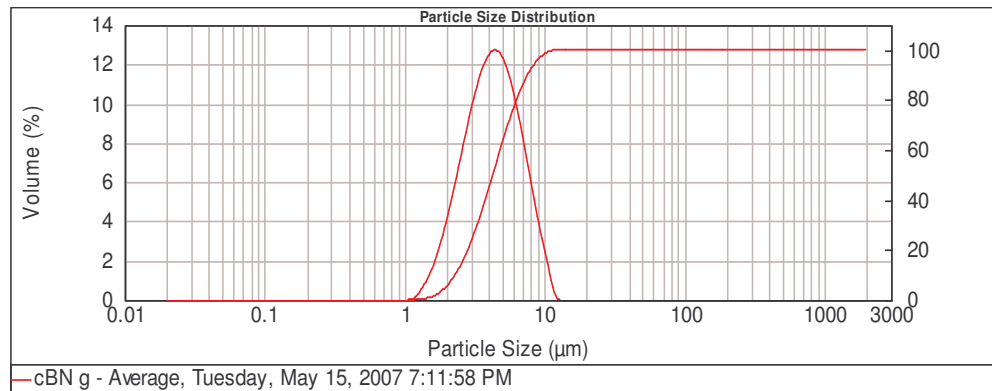


Fig. 4.5: Particle size distribution of raw powder cBN "C4 cBN powder ex Element Six".

4.1.3 Surface Area

AKP-50 alumina and cBN powders were analysed using the multipoint Brunauer, Emmett and Teller (BET) model (Autosorb-1, Quantachrome Co.) through nitrogen adsorption. Figure 4.6 and 4.7 show the adsorption isotherms of these powders respectively, which illustrate the volume of gas adsorbed or desorbed from the surface of the powder as a function of the relative pressure applied.

BET measurement revealed a specific surface area of $10.3 \text{ m}^2/\text{g}$ for Al_2O_3 AKP-50 and $1.5 \text{ m}^2/\text{g}$ for cBN $d_{90}=3.21 \text{ }\mu\text{m}$. AKP-50 alumina with particle size of $0.1\text{-}0.3 \text{ }\mu\text{m}$ has a specific surface area higher than cBN with a particle size of $3\text{-}4 \mu\text{m}$.

The alumina and cBN powders have isotherms of type II which is the standard form of isotherm obtained with non-porous adsorbents. The start of the linear central section of the isotherm is assumed to indicate the relative pressure at which monolayer coverage is complete. There is a shift between the intrusion and extrusion curves (hysteresis) and a portion of the gas is retained within the sample. The desorption branch in the hysteresis loops lies to the left of the adsorption branch. The measured surface areas were in excellent agreement with those determined by the suppliers.

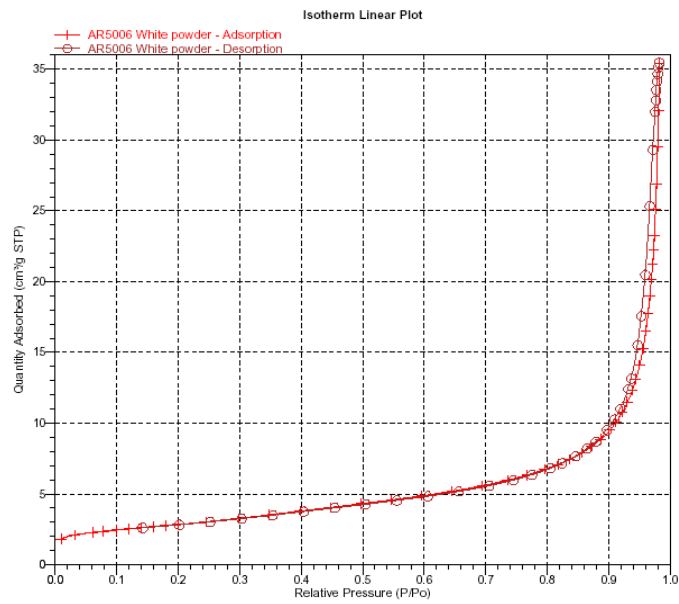


Fig. 4.6: Adsorption and desorption Isotherm linear plot of alumina AKP-50.

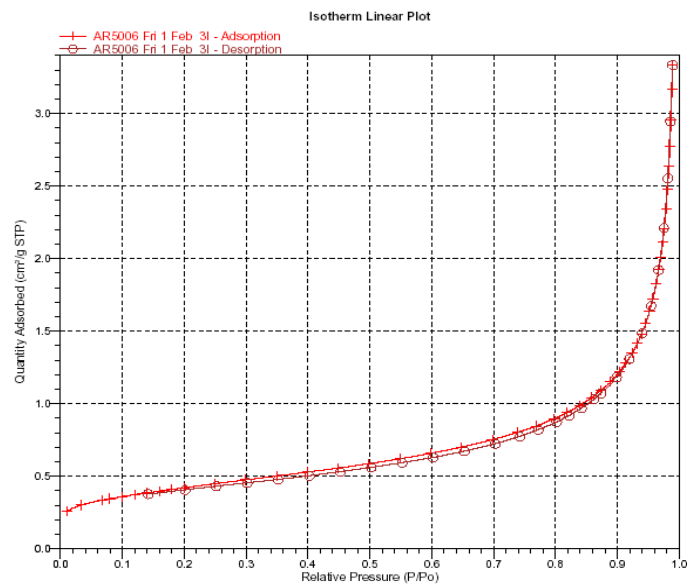


Fig. 4.7: Adsorption and desorption Isotherm linear plot of cBN grade 3.

4.2 Optimization of a suspension for gelcasting

4.2.1 Solid loading

For the solid loading effect study, all the suspension were controlled at pH=8.5 and a solid loading of 50 vol% and 1wt% of Al_2O_3 for the APAA concentration. Figure 4.8 shows that as the Al_2O_3 solid loading increases from 10 to 60 vol%, the APAA adsorbed onto Al_2O_3 increase. The more favourable APAA adsorption onto the Al_2O_3 surfaces is at a lower pH. During the Al_2O_3 solids loading adjustment, Al_2O_3 and APAA additions shift the suspension pH to a more acidic condition from pH 8.5. This suspension adjustment process promotes the APAA adsorption onto Al_2O_3 . After the APAA adsorption under the more acidic condition, the final adjustment of pH to 8.5 does not change the bonding between APAA and Al_2O_3 and the higher APAA adsorption. From Figure 4.8 we observe that the viscosity increase with the solid loading in both cases(with and without dispersant ammonium polyacrylic acid APAA). Figure 4.8 shows that the suspension without dispersant (APAA) has a reasonably low viscosity for a solid loading below 40 vol% solids and the one with dispersant shows a reasonably low viscosity and a good dispersion from 20 to 60 vol% solids loading. It can also be easily observed that the viscosity is a strong function of the Al_2O_3 solids loading. With an increase in solids loading, the viscosity increases. Generally, there is a complex nonlinear relationship between viscosity and solids volume fraction, which is closely related to many factors, such as the continuous phase viscosity, particle-size distribution, and particle shape, etc. The curves in Figure 4.8 have the typical shape of a plot of solids loading versus viscosity: low viscosity at low solids loading and sharp increase at high solids loading. There must come a time, as more and more particles are added when suspensions “jam up”, giving continuous three-dimensional contact throughout the suspension, thus, making flow impossible, i.e. the viscosity tends to infinity. The particular phase volume at which this happens is called the maximum packing fraction ϕ_m [37]. Adding a little more Al_2O_3 to approximately 52 vol% will lead to a “solidified” slurry, thus, the viscosity will increase sharply and make it practically impossible to measure

the viscosity by a rheometer with a concentric-cylinder setting. The ϕ_m value is thus determined to be 52 vol%. Adding 1 wt% of APAA increase ϕ_m to about 65 vol%, suggesting that APAA is very effective in increasing Al_2O_3 solids loading. The relationship between the viscosity and the solids volume percentage for monodispersed suspension can be described by Krieger-Dougherty (K-D) model as:

$$\eta = \eta_0 \left(1 - \frac{\phi}{\phi_m} \right)^{-[\eta] \phi_m} \quad (4.1) [37]$$

Where η is the viscosity of the suspension and η_0 is the viscosity of the solvent. The true volume fraction of the powder dispersed in the suspension is represented by the variable ϕ . The intrinsic viscosity $[\eta]$ of the suspension is a function of particle geometry; a value of 2.5 is appropriate for spherical particles.

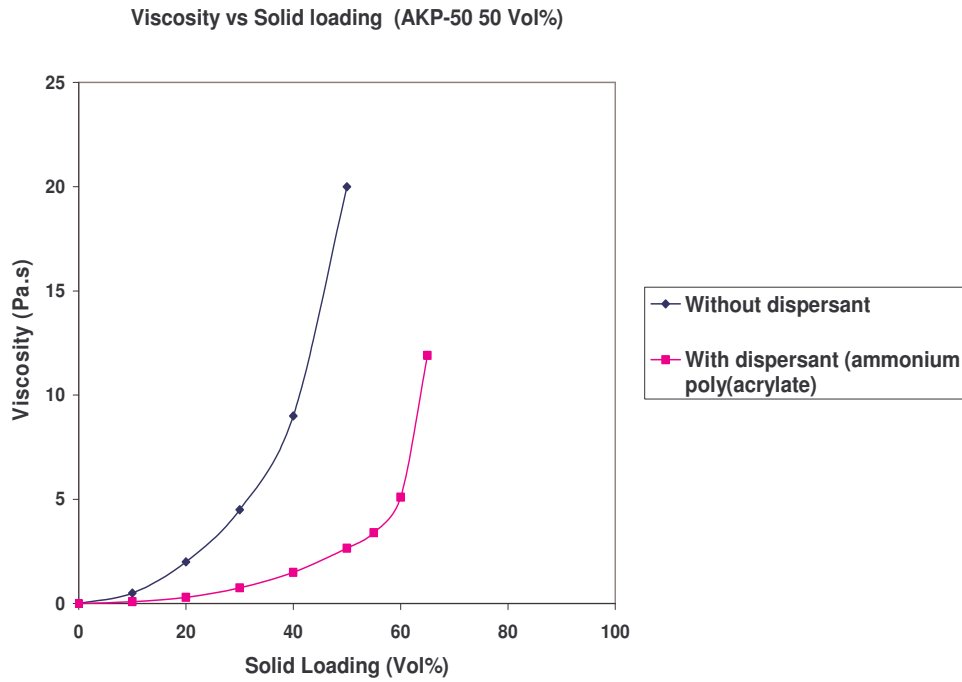


Fig. 4.8: Variation of apparent viscosity versus volume concentration of alumina AKP-50.

4.2.2 Effect of dispersant Ammonium Poly (acrylic acid) (APAA) on the AKP-50 Alumina and Alumina-cBN slurry

To study the APAA concentration effect on its adsorption onto Al_2O_3 AKP-50 in high solids loading suspension, the solids loading of the suspension was fixed at 50 vol% while the APAA concentration was varied between 0.5 and 3.5 wt% of Al_2O_3 as shown in Figure 4.9a and 4.9b. As the APAA concentration increases up to 1wt% of Al_2O_3 of APAA concentration, the APAA amount adsorbed onto Al_2O_3 particles also increases leading to a decrease in suspension viscosity at pH 8.5, indicating that the dispersibility of the colloidal particles was increased by the adsorption of APAA. Further addition resulted in increased viscosity due to saturation of the particle surfaces with adsorbed APAA, which eliminates the dependence of the suspension rheology on the APAA concentration. When the adsorbed APAA amount became larger than the saturated amount this leads to increase in viscosity, this result may be interpreted by the coagulation of the dispersed colloid particles through free APAA.

Figure 4.9a shows the viscosity measurements at shear rate range $0\text{--}100\text{ S}^{-1}$ for the suspension of 50 vol% solids loading and different APAA concentrations. Stable concentrated suspensions usually exhibit shear thinning behaviour because of a perturbation of the suspension structure by shear [38]. At low shear rates, the suspension structure is similar to the equilibrium structure at rest, because thermal motion dominates over the viscous forces. At high shear rates, the viscous forces affect the suspension structure more and shear thinning occurs. It can be seen from the figure that the suspension had the lowest viscosity at 1wt% of Al_2O_3 APAA concentration. As the APAA content increases, the viscosity increases. The viscosity increase at a low APAA concentration can be explained by a shortage of APAA adsorption onto Al_2O_3 (incomplete APAA coverage of Al_2O_3) and the resultant bridging flocculation. A balance needs to be maintained for the APAA adsorbed onto Al_2O_3 particles and the free APAA dispersant in the suspension. The results in Figure 4.9a and Figure 4.10a serve as an important

guide in optimizing the dispersion conditions. For the studied system, the optimal APAA content is 1wt% of Al_2O_3 and for Al_2O_3 -cBN as well.

Viscosity of Alumina AKP-50 slurry with 50 vol.% solids loading

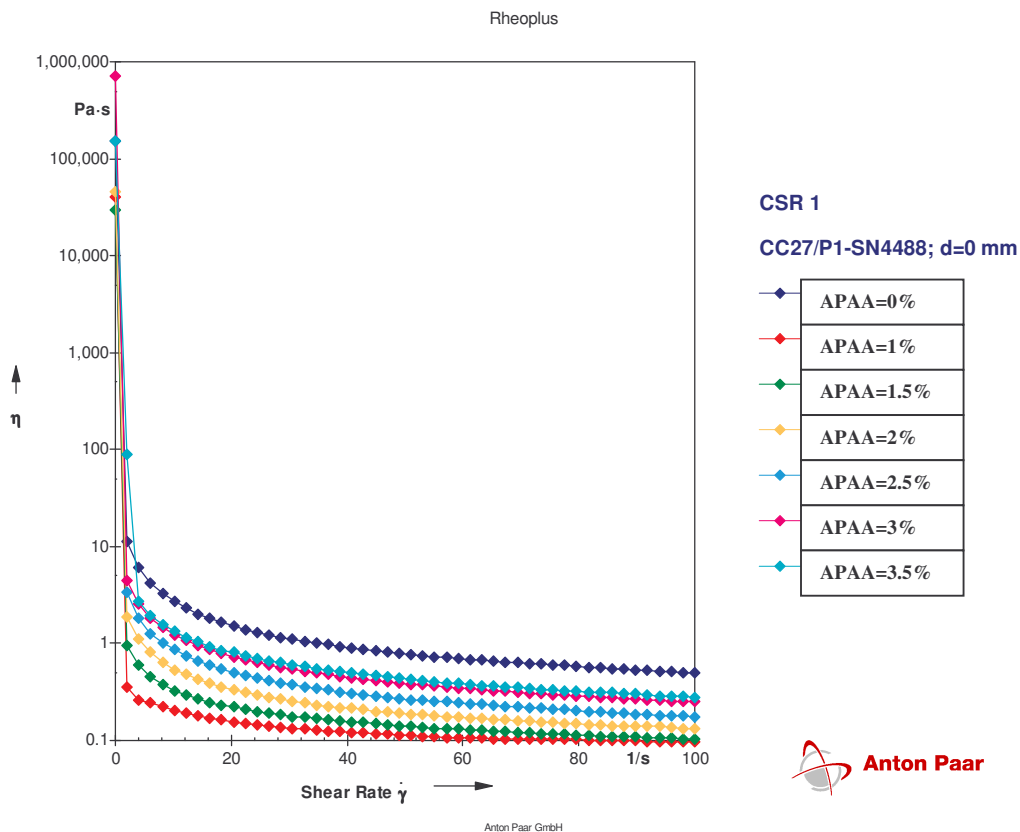


Fig. 4.9a: viscosity of a alumina AKP-50 slurry as a function of dispersing agent ammonium poly(acrylic acid) (APAA) for gelcasting exhibiting shear thinning behaviour.

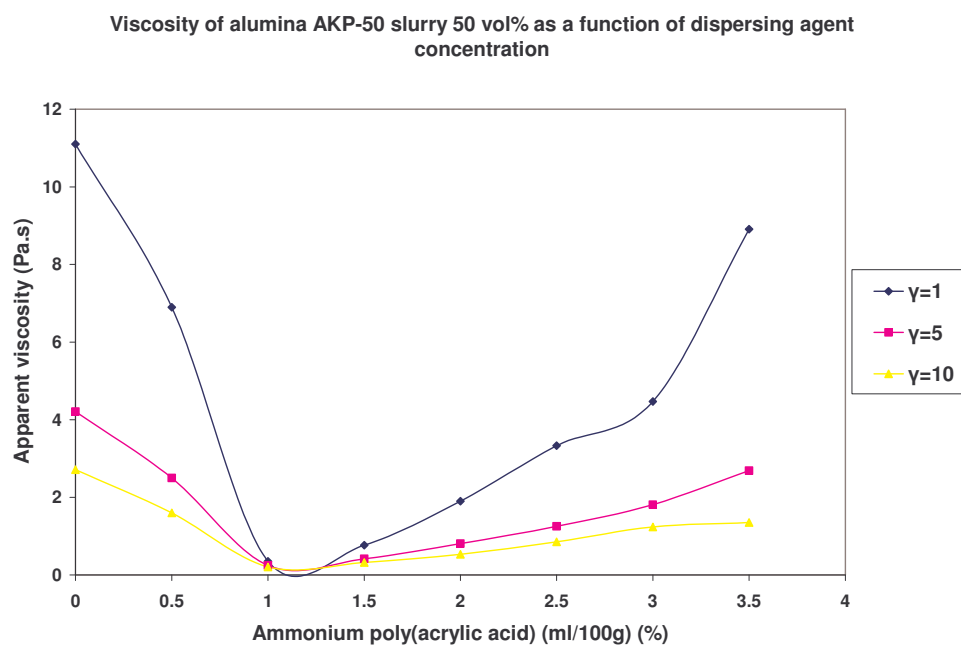


Fig. 4.9b: viscosity of a alumina AKP-50 slurry as a function of dispersing agent ammonium poly(acrylic acid) (APAA).

Viscosity of Alumina-cBN slurry with 50 vol.% solids loading

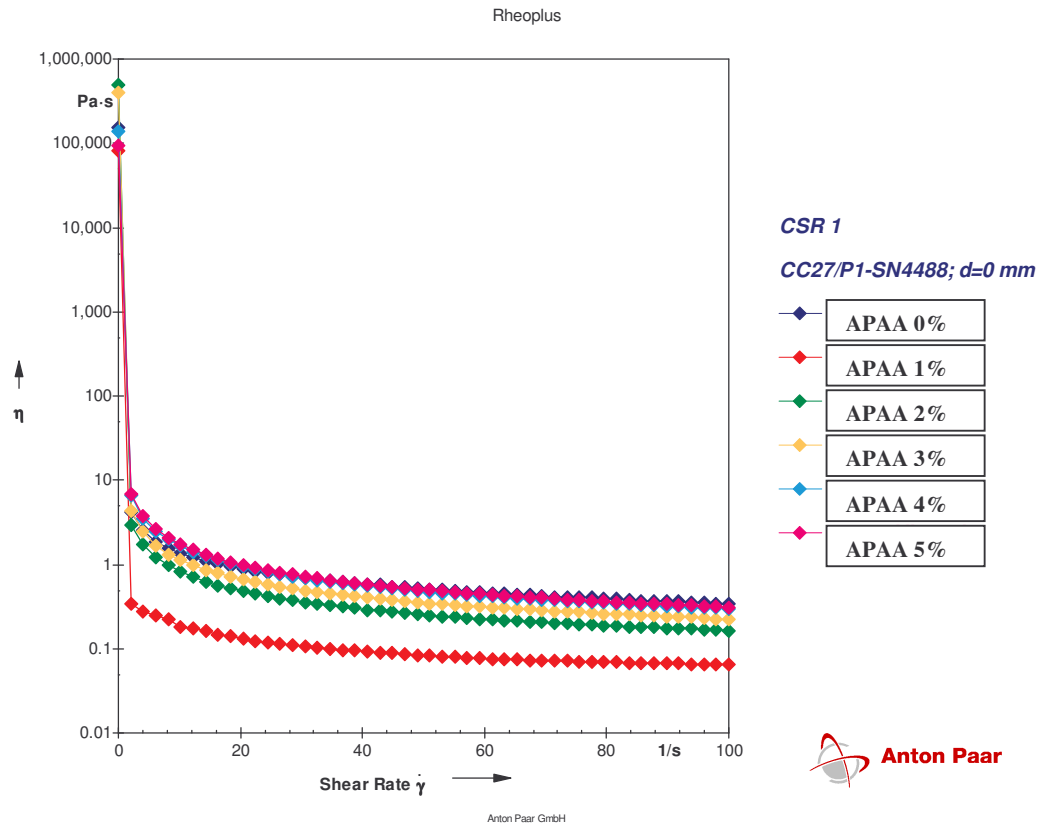


Fig. 4.10a: Viscosity of Al_2O_3 -cBN in terms of shear rate, the parameter is the amount of dispersant ammonium polyacrylic acid (APAA) for gelcasting exhibiting shear thinning behaviour.

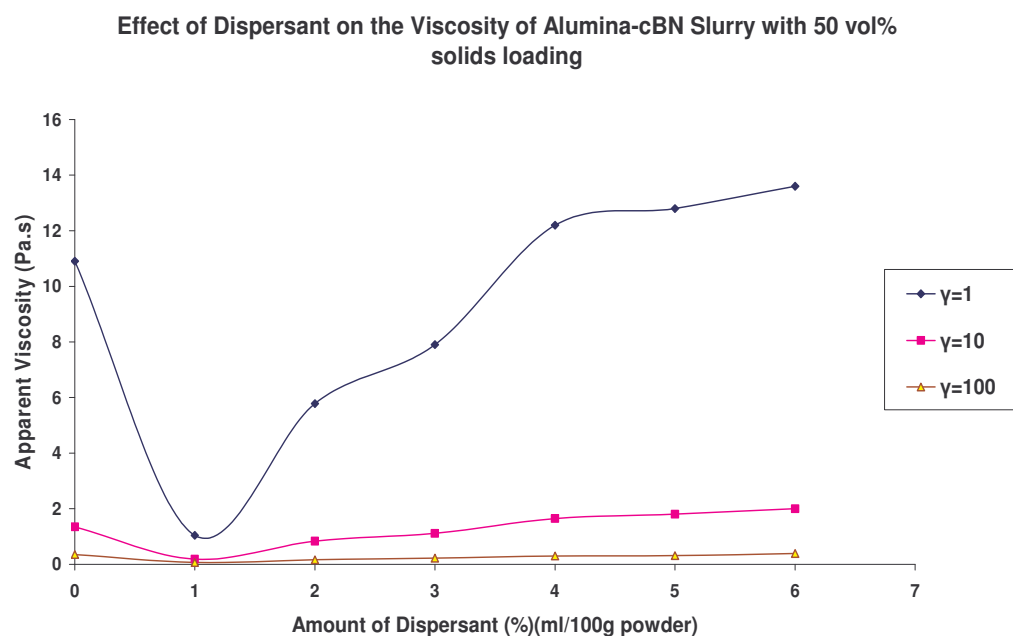


Fig. 4.10b: Viscosity of Al_2O_3 -cBN in terms of the amount of the dispersant ammonium polyacrylic acid (APAA). The parameter is the shear rate.

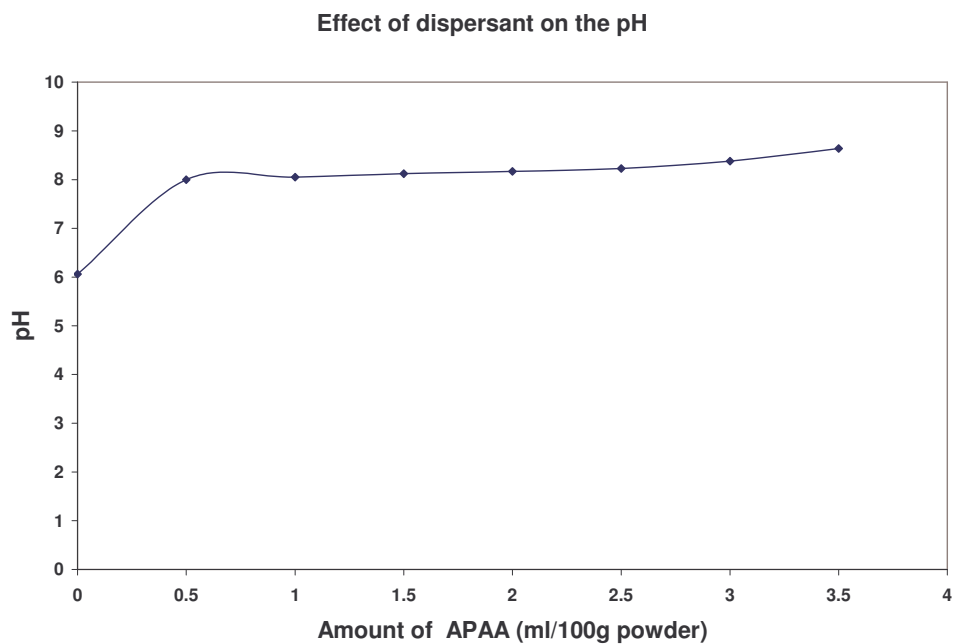


Fig. 4.11: Effect of addition of dispersant APAA on the pH of the Al_2O_3 suspension.

4.2.3 Rheological Properties of HEMA-PVP system

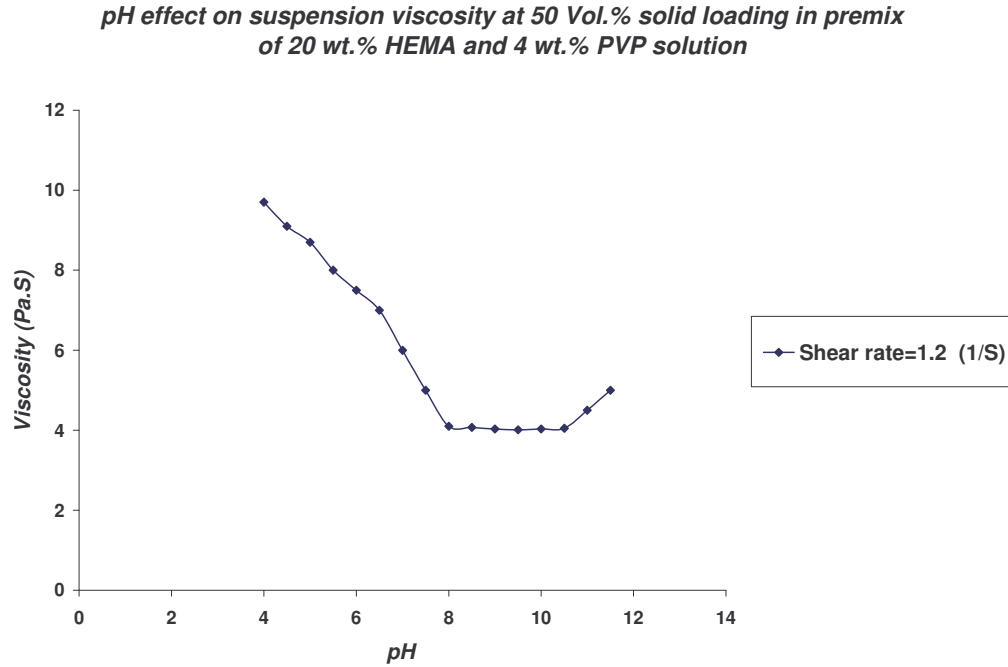


Fig. 4.12: pH effect on suspension viscosity at 50 vol.% solids loading and 1wt% of Al_2O_3 ammonium poly(acrylic acid) concentration.

The effect of the pH on the adsorption of ammonium poly acrylic acid (APAA) onto Al_2O_3 particles: Based on the APAA concentration effect on the suspension stability, a APAA concentration of 1 wt% of Al_2O_3 was used for this study, while the solids loading was maintained at 50 vol.%. The pH was varied from 4 to 12. As shown in Figure 4.12, At low pHs, APAA tends to have more train configuration in the suspension. At pH 8-10, APAA has the highest adsorption, this the most desirable pH range for stabilizing the Al_2O_3 suspension. At pH 8-10, APAA have more loop and tail configurations, which provides electrosteric stabilization. When the pH is too high, APAA adsorption onto Al_2O_3 particles is too low, depletion flocculation results, and viscosity increases.

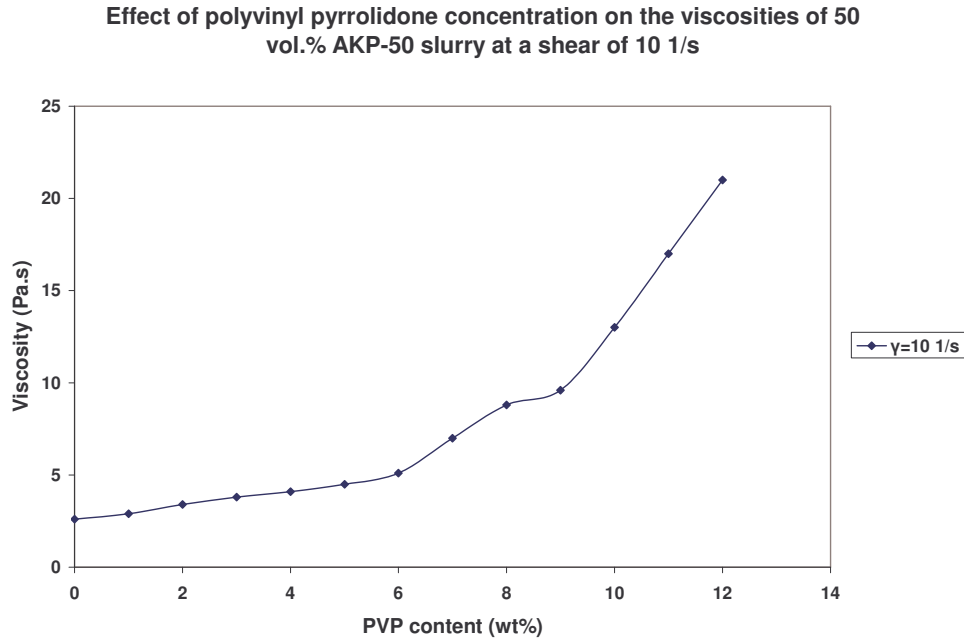


Fig. 4.13: Influence of polyvinyl pyrrolidone concentration on the viscosities of 50 vol.% Al_2O_3 suspension at shear rate of 10 S^{-1} .

Because PVP is a macromolecule (molecular weight of $\sim 40\,000$), the addition of PVP should also have a more or less steric effect that can prevent particles from aggregating. This may be the reason for PVP's small influence on the suspension viscosity. In fact, PVP is also used as a steric dispersant for inorganic and organic materials [19,24]. Further addition of PVP above 6 wt% will strongly increase the slurry viscosities as shown in the Figure 4.13. Addition of a polymer to the suspension can have various and subtle effects on surface force of the particle depending on the chemical nature of the polymer, the solution, and the particle, as well as on the polymer molecular weight, particle concentration, etc. Bridging flocculation is unlikely to occur here for PVP because the polyelectrolyte dispersant is dominant on the particle surface. Therefore, another type of flocculation for soluble polymers, depletion flocculation, should be the reason for the increase of viscosity at a higher PVP concentration, since the osmotic pressure difference in the depletion flocculation mechanism will be enhanced at a higher polymer concentration.

4.2.4 Zeta potential

Zeta potential values of different alumina and alumina-cBN aqueous suspensions at different pH values are shown in Figure 4.14a and Figure 4.14b. The zeta potential value of Al₂O₃-HEMA suspension change from -9 mV at pH=1 to -45.35 mV at pH=12.

Note that by adding 1 wt% APAA and 2 wt% PVP results in much more negative potential values. A value of -55.76 mV for Al₂O₃-HEMA suspension at pH=8 is moved to about -70 mV with a addition of APAA and to -81 mV with addition of 2 wt% PVP. As shown in Figure 4.14a, the zeta potential is negative in spite of the pH changing to values below the IEP of alumina. This is not common behaviour for oxides [39], which are normally positively charged below their zero charge point as a result of a reaction such as



Therefore, it is likely that as the particles surface was covered with HEMA monomers, the adsorption of NH₄⁺ ions was inhibited, which prevented the positive charges in the evaluated pH range from developing. This means that the monomer adsorption on the powder surface might have changed alumina pK_a as previously observed in a couple of materials [40]. In fact, it has been shown that the ability of the adsorbate in changing the particles surface charge increases with the number of dissociable groups and that molecules with only one functional group would not be able to change the surface charge[41]. Although each acrylic acid molecule has only one carboxylate group, it is expected that some dimmers and/or oligomers are found in the monomer solution. These molecules with additional carboxylate groups might induce a small negative surface charge in a pH range below the IEP[42].

At this stage, the only effect of adding polyelectrolyte was a reduction in the dissociation of carboxylate groups which were not involved in the attachment of dimmers and oligomers to the surface, increasing the nondissociated (R- COOH)

fraction. As the pH increased, the activity of the deflocculant became high enough to withdraw the monomers from the alumina surface, which were replaced by the polyelectrolyte. A gradual increase in the negative ζ potentials of the powders up to pH=8 for Alumina suspension in 20 wt% HEMA premix gave rise to a high negative zeta potential and the suspensions are colloidally stable at pH=8. For alumina in 20 wt% HEMA premix + 1wt% APAA the zeta potential maximized at pH=10, which can provide better colloidal stability, and for alumina in 20 wt% HEMA premix + 1wt% APAA + 2 wt% PVP the zeta potential is maximized at pH=8 which also can provide colloidal stability. Consequently, the zeta potential changed from -49.43mV to -54.22 mV with addition of 1wt% APAA and to -79.05 mV with addition of 2wt% PVP at pH=6. Since the polyelectrolyte (APAA) dissociates only partially in this pH range (2-6), the dispersing effectiveness is limited, and higher charges are not expected. In addition, a large fraction of the alumina surface sites is positively charged in this pH range, counterbalancing part of the polymer negatively charges. Higher zeta potential values would be expected if the pH were increased. Nonetheless, the higher ionic strength would limit the zeta potential, comparatively to the values observed in suspensions prepared with either HEMA or plain water.

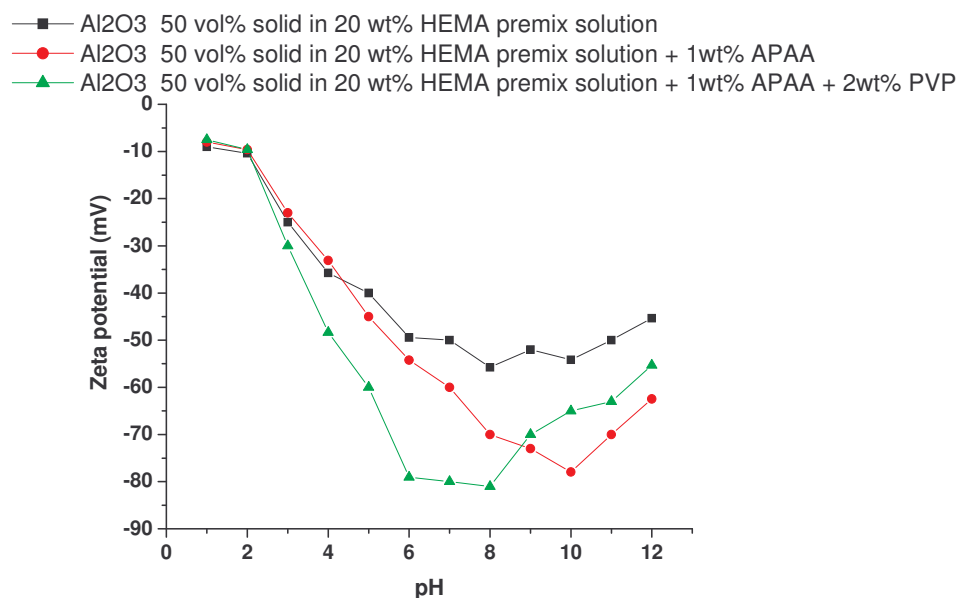


Fig. 4.14a: Comparison of pH value dependence of zeta-potentials for different alumina suspensions.

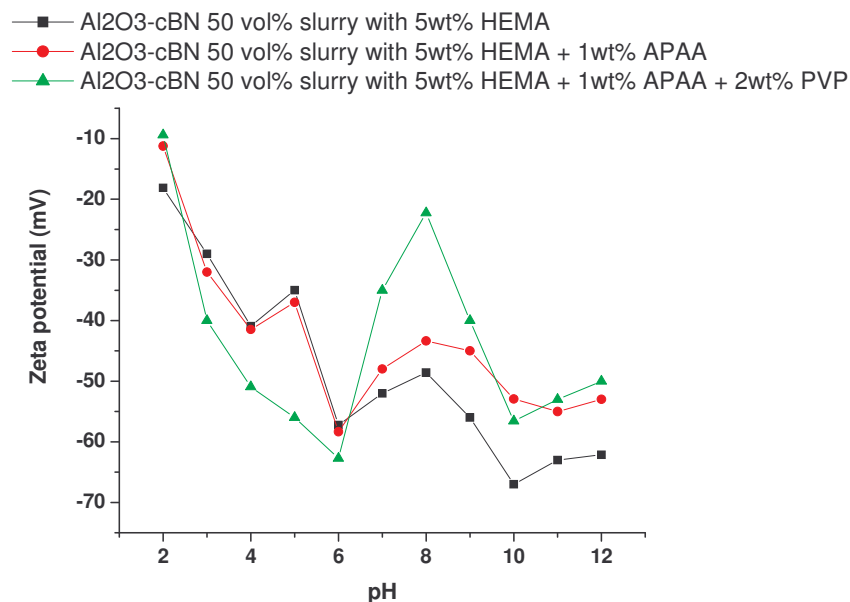


Fig. 4.14b: Comparison of pH value dependence of zeta-potentials for different alumina-cBN suspensions.

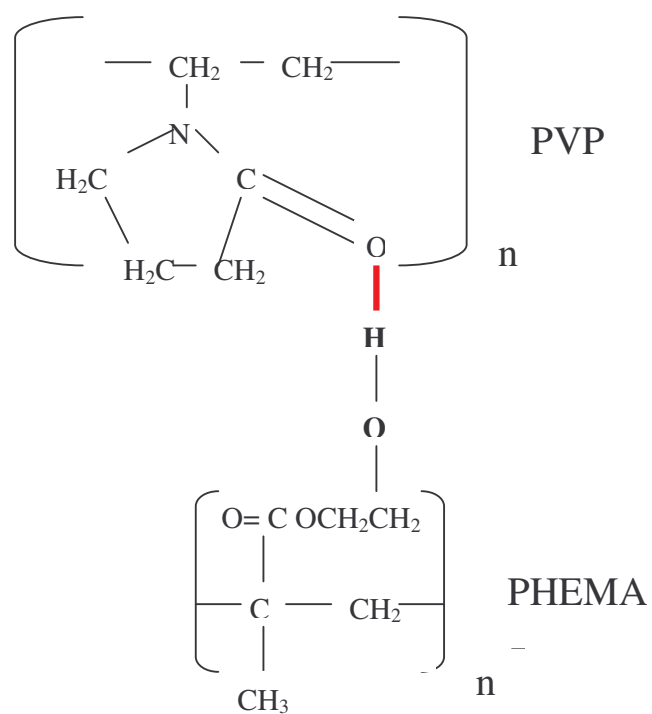


Fig. 4.15: Illustration of molecule structures of polyvinyl pyrrolidone and poly-2-hydroxyethyl methacrylate and hydrogen bonding between the two molecules [43].

Table 4.1a: Composition of slurry for gelcasting

No	Preparation							
	Vol% powder (Al ₂ O ₃ Akp-50)	Monomer/ Crosslinker	Ratio	Dispersant	Defoaming agent	pH	Mixing time	Deairing under vacuum
1	50	HEMA/ MBAM	4:1	APAA 1wt%	Silicone oil 1vol%	8.5	24 h	10 min
2	60	HEMA/ MBAM	4:1	APAA 1wt%	Silicone oil 1 vol%	8.5	24 h	10 min
3	50	HEMA/ MBAM	6:1	APAA 1wt%	Silicone oil 1 vol%	8.5	24 h	10 min
4	60	HEMA/ MBAM	6:1	APAA 1wt%	Silicone oil 1 vol%	8.5	24 h	10 min
5	50	HEMA/ MBAM	4:1	APAA 1wt%	Tributyl phosphate 1 vol%	8.5	24 h	10 min
6	60	HEMA/ MBAM	4:1	APAA 1wt%	Tributyl phosphate 1 vol%	8.5	24 h	10 min
7	50	HEMA/ MBAM	6:1	APAA 1wt%	Tributyl phosphate 1 vol%	8.5	24 h	10 min
8	60	HEMA/ MBAM	6:1	APAA 1wt%	Tributyl phosphate 1 vol%	8.5	24 h	10 min
9	50	HEMA/ MBAM	4:1	APAA 1wt%	n-octanol 1 vol%	8.5	24 h	10 min
10	60	HEMA/ MBAM	4:1	APAA 1wt%	n-octanol 1 vol%	8.5	24 h	10 min
11	50	HEMA/ MBAM	6:1	APAA 1wt%	n-octanol 1 vol%	8.5	24 h	10 min
12	60	HEMA/ MBAM	6:1	APAA 1wt%	n-octanol 1 vol%	8.5	24 h	10 min

Table 4.1b: Composition of slurry for gelcasting

No	Preparation								
	Vol% powder (Al ₂ O ₃ Akp-50)	Monomer/ Crosslinker	Ratio	Dispersant	PVP content Wt%	Anti foaming agent	pH	Mixing time	Deairing under vacuum
20	50	HEMA/ MBAM	4:1	APAA	2	n-octanol 1 vol%	8.5	24 h	10 min
21	60	HEMA/ MBAM	4:1	APAA	2	n-octanol 1 vol%	8.5	24	10 min
22	50	HEMA/ MBAM	4:1	APAA	4	n-octanol 1 vol%	8.5	24	10 min
23	60	HEMA/ MBAM	4:1	APAA	4	n-octanol 1 vol%	8.5	24	10 min
24	50	HEMA/ MBAM	4:1	APAA	6	n-octanol 1 vol%	8.5	24	10 min
25	60	HEMA/ MBAM	4:1	APAA	6	n-octanol 1 vol%	8.5	24	10 min

4.2.5 Adsorption of ammonium poly (acrylic acid) on the surface of oxide particle

The addition of Ammonium poly (acrylic acid) as dispersant lead to electrosteric stabilization of the suspension. The polymer APAA see Figure 4.16 below with its ionisable group $-\text{COO}^-\text{NH}_4^+$ develop electrostatic charges by dissociation. The dissociation of the polymer as well as their adsorption is strongly influenced by the properties of the solvent and the particle surfaces.

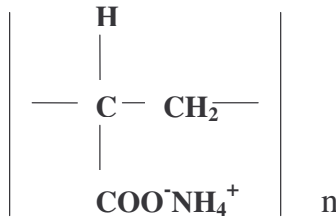


Fig. 4.16: Schematic diagrams showing the polymer segments of ammonium poly(acrylic acid) (APAA) [24].

The functional group of APAA can exist as COONH_4 or dissociated to $\text{COO}^-\text{NH}_4^+$. The dissociation reaction can be written in a general form as



Depending on the pH and the ionic concentration of the solution, the fraction of the functional group which is dissociated (i.e., COO^-) and which is not will vary[20]. As the fraction α of acid groups COOH dissociated increases from 0 to 1, the charge on the polymer varies from neutral to highly negative. As the pH increases, the extent of dissociation and the negative charge of the polymer

increases. At a pH greater than 8.5, the polymer is highly negative with $\alpha=1$, with α being the fraction of acid group dissociated. Under these conditions, the free polymer is in the form of relatively large expanded random coils due to the repulsion between the charged segments. As the pH decreases, the number of negative charge decreases, with the polymer being effectively neutral at a pH of 5. In the neutral condition, the polymer forms small coils or clumps.

Adsorption of polyelectrolyte onto the particle surface is commonly dominated by electrostatic interactions and is often strongly favored if the particle surface and the polyelectrolyte have opposite charges. As discussed earlier, the surface charge of the oxide particles dispersed in aqueous solvents depends on the pH of the suspension. We see that considerable electrostatic attraction should occur between the negatively charged polyelectrolyte and the positively charge Al_2O_3 , particularly in the pH range of ~ 5 to 8.5.

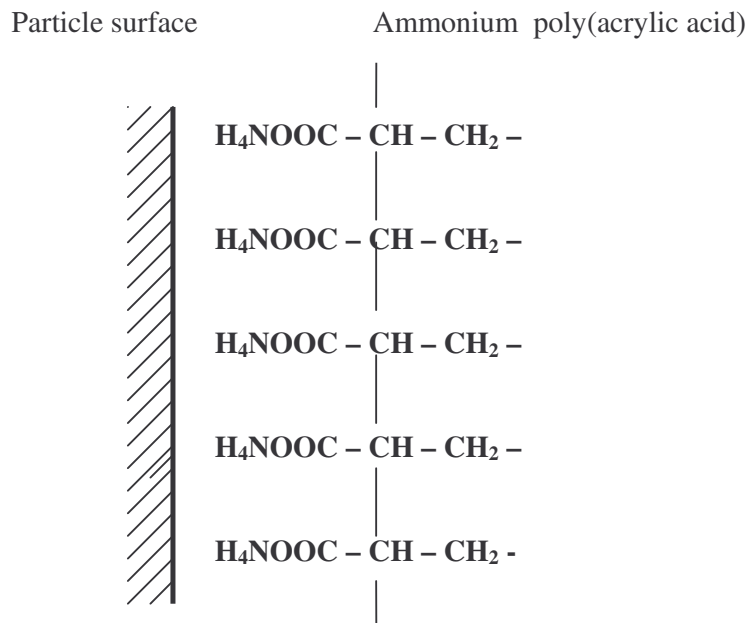


Fig. 4.17: Model for the adsorption of ammonium poly (acrylic acid) on an oxide Particle.

4.3 Gelation

According to the principles of free radical polymerisation, the amount of initiator has an important influence on polymerisation. First the initiator forms free radicals; it then reacts with the monomer as well as initiating polymerisation. Catalysts may enhance the polymerisation. Catalysts may enhance the polymerisation rate as it can be seen on the figure 4.18. In the present study the amount of catalyst was fixed at half the amount of initiator.

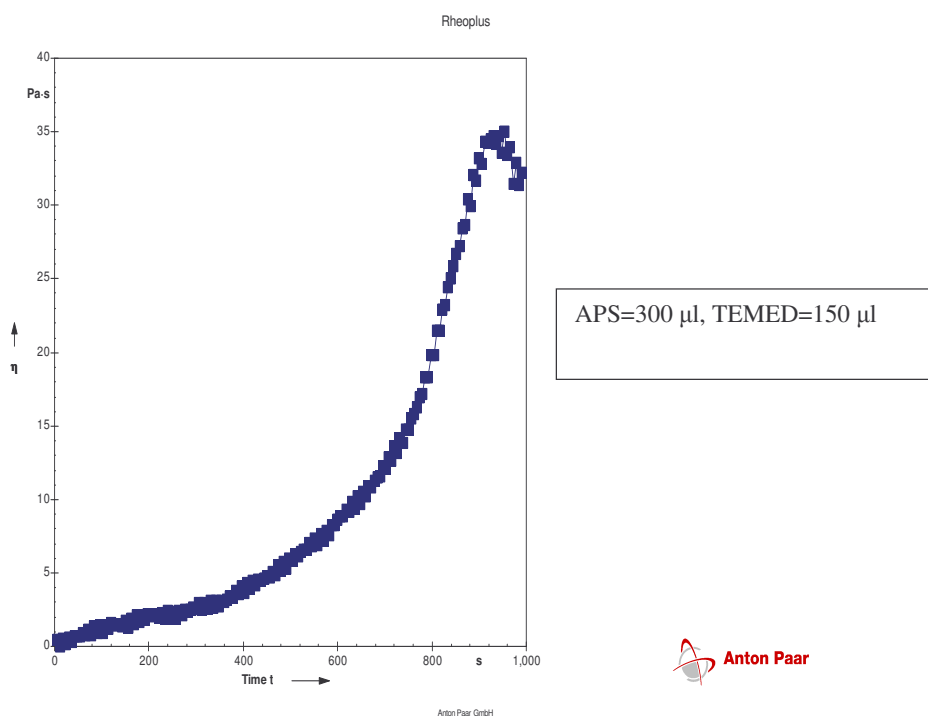


Fig. 4.18: Viscosity variation with time of AKP-50 alumina slurry in presence of initiator APS and catalyst TEMED at shear rate of 5.

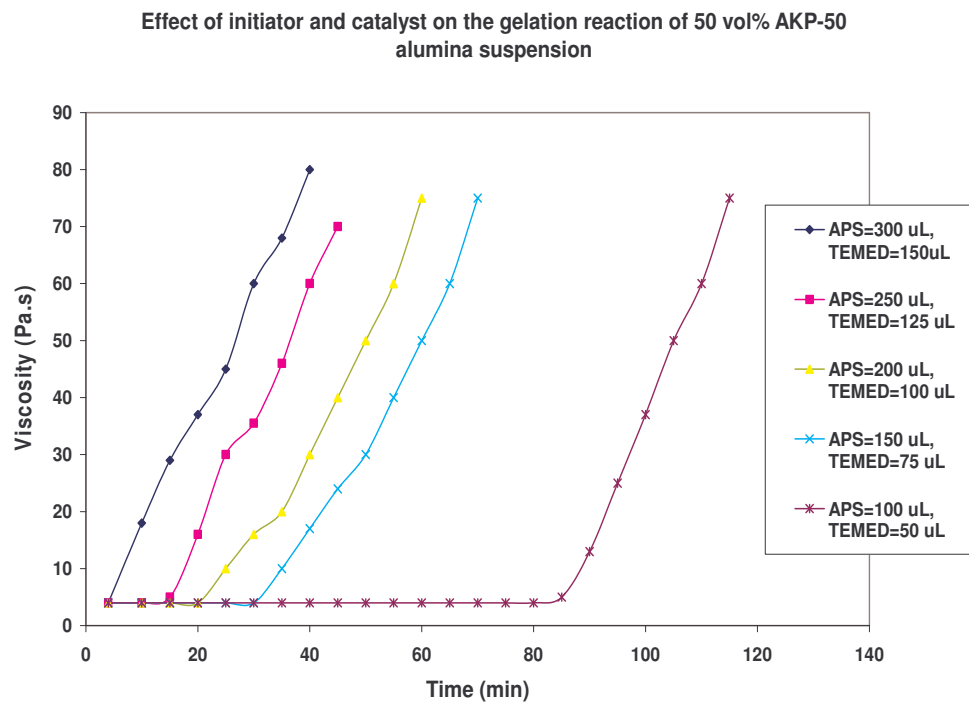


Fig. 4.19: Viscosity variation with time of AKP-50 alumina slurry in presence of different amount of initiator and catalyst.

Table 4.2: Effect of initiator and catalyst amount on gelation time of alumina suspensions (shear rate=5).

<i>Initiator, μL</i>	<i>Catalyst, μL</i>	<i>Gelation time, min</i>	<i>Ratio monomer crosslinker</i>	<i>Gelation status after 1 h</i>
100	50	80	4:1	Incomplete
150	75	35	4:1	Complete
200	100	24	4:1	Complete
250	125	13	4:1	Complete
300	150	6	4:1	Complete

Figure 4.19 shows the effect of initiator content on gelation time for 50 vol% Al_2O_3 suspensions containing 4.5 wt% PVP at a temperature of 50°C. Thus, gelling characteristics of alumina slurries were characterized by the time dependence of the viscosity. The viscosity change was measured at 5 s⁻¹. The slurry viscosity increases gradually in first few minutes and then rapidly with time as it can be seen in the Figure 4.18. This indicates that, the formation polymer(gel) structure is taking place due to rapid bridging. It can be seen that gelation time decreased rapidly with increasing amount of initiator. When a larger amount of initiator was used, the suspension gelled and solidified rapidly, making control of the suspension gelation rate difficult. When a small amount of initiator was used the gelation of suspensions occurred relatively slowly and many hours were required.

It was also found that a homogeneous green body was obtained when 200 µL of a 5 wt% aqueous solution of initiator (100 µL catalyst) was added to 20 mL of suspension. The gelation time dependence of AKP-50 alumina slurry in presence of different concentrations of initiator and catalyst is shown in Table 4.2. The optimum gelation time is found to be at 24 min which correspond to amount of 200 µL initiator (100 µL catalyst).

4.4 Deairing

Improvement of deairing with Defoamings aids

One of the critical problem encountered in gelcasting technology was the presence of pores left by the air bubbles that were not eliminated by the deairing process. The addition of an additive called antifoam, or defoaming aid in order to eliminate bubbles from a slurry can be used to improve the deairing process.

Initially the problem of low density was achieved due to presence of internal voids in the material that reduce the mass, leading to the formation of defects. The apparent density is less than the ultimate density of the solid phase. This problem can be overcome by associating to the deairing under mechanical pump vacuum a deairing aid called antidefoam, or defoaming aid (defoamer).

We have tested three defoamers: tributyl phosphate, silicone oil and n-octanol. The introduction PVP in the formulation of slurry has contributed as well to improve the green density of the gelcast. The PVP is likely to form a more complicated network structure through hydrogen bonding with HEMA resulting in an intimate mix of polymer chains[44]. The intermolecular hydrogen bonding between PVP and PHEMA (poly hydroxyethyl methacrylate) has several effects[45] : it can act as a barrier for diffusion of water and oxygen, it can increase the equilibrium water content of the hydrogel, and in turn can prevent phase separation, which is the origin of the low-strength samples. Figures 4.20a, 4.20b and Figure 4.21a show respectively the microscopic and SEM structures of sintered gelcast samples which slurries were deaired using defoaming aid respectively with silicone oil and tributyl phosphate. It can be seen from these images the presence of pores left by bubbles. We observe from Figures 4.20c, 4.20d and Figure 4.21b respectively microscopic and SEM structures of sintered gelcast samples which slurries were deaired using defoaming aid n-octanol. It can be seen that bubbles were more or less removed from the slurries therefore the structures appear homogeneous.

Microscopic images

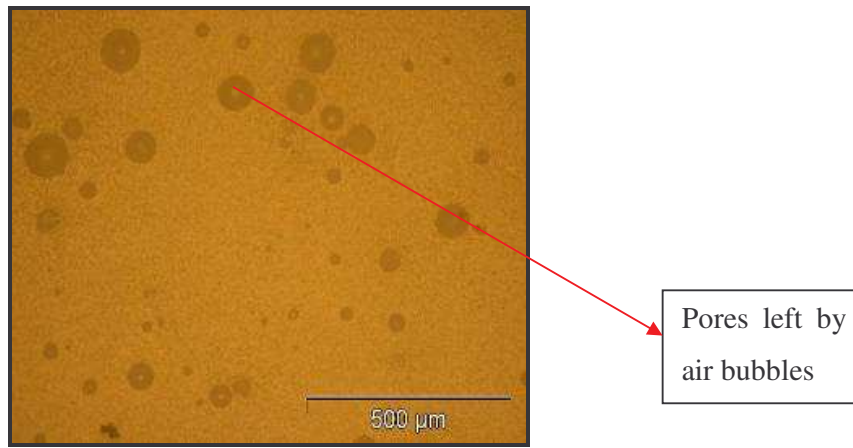


Fig. 4.20a: Microscopic image of sintered alumina gelcast part 50 vol.% solids loading, with silicone oil 1 vol% of Al_2O_3 as defoaming agent.

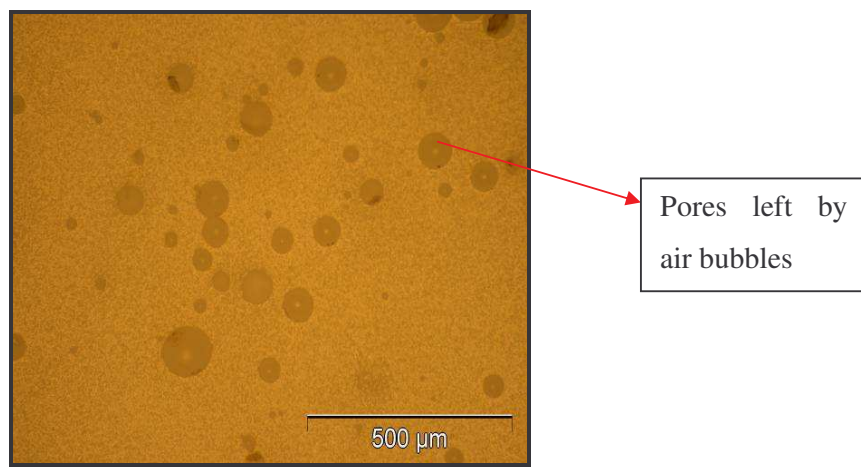


Fig. 4.20b: Microscopic images of sintered alumina gelcast part 50 vol.% solids loading, with tributyl phosphate 1 vol% of Al_2O_3 as defoaming agent.

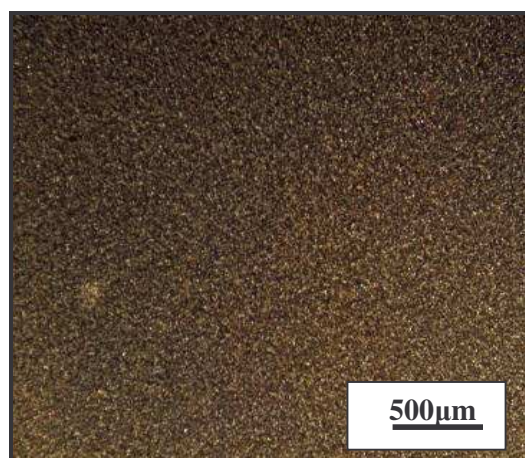


Fig. 4.20c: Microscopic image of sintered alumina gelcast 50 vol.% solids loading, with n-octanol 1 vol% of Al_2O_3 as defoaming agent.

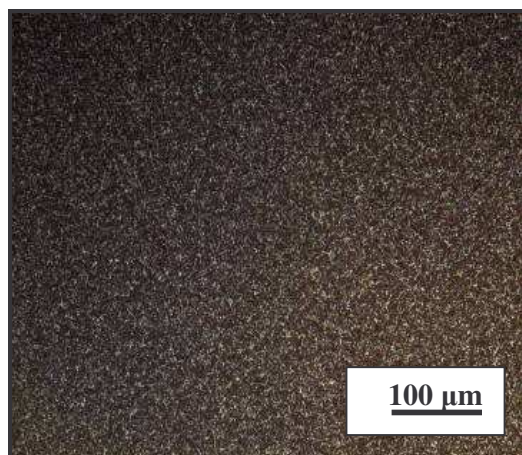
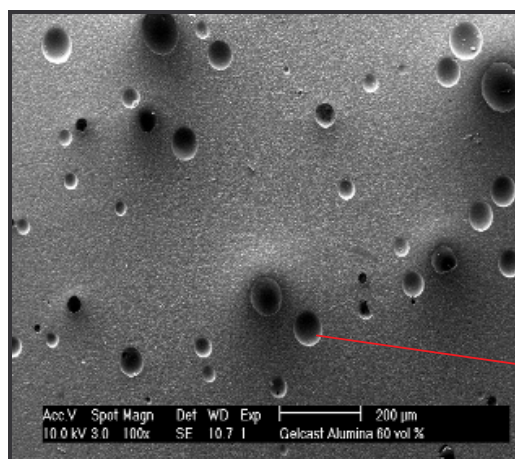


Fig. 4.20d: Microscopic image of sintered alumina gelcast 50 vol.% solids loading, with PVP 4 wt% of Al_2O_3 and n-octanol 1 vol% of Al_2O_3 as defoaming agent.

SEM images



Pores left by
air bubbles

Fig. 4.21a: SEM image of sintered alumina gelcast part 50 vol.% solids loading, with tributyl phosphate 1 vol% of Al_2O_3 as defoaming agent.

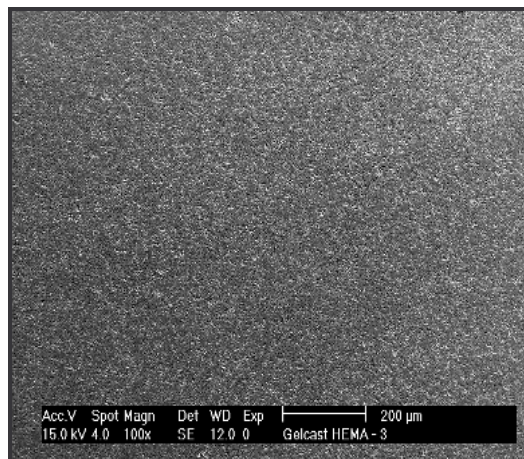


Fig. 4.21b: SEM image of sintered gelcast 50 vol.% solids loading, with n-octanol 1 vol% of Al_2O_3 as defoaming agent.

4.5 Drying

The wet body was dried in a humidity-controlled chamber because drying without humidity results in cracking due to non-uniform shrinkage. The drying weight-loss curves for specimens prepared with 5 wt% monomer and 50 vol% alumina AKP-50 content were dried at 30°C and different humidity conditions from 30%RH to 90%RH are shown in Figure 4.22 as plots of the weight loss vs time. We observe that the drying weight-loss increases when the humidity decreases, on reducing the humidity content of the drying air, water is removed from the drying part at a higher rate.

The drying process can be classified into three stages[20]. In the initial stage (constant rate period) the water is evaporated at a constant rate via capillary force to the surface of the green body. The green body thus shrinks at the rate of water evaporation. The initial linear drying range in the present study, the first 10 h, was confirmed as such a constant rate drying period. The transition between the intermediate stage (falling rate period) and the final stage (polymer diffusion period) appears to occur at around 40 h.

The evaporation of liquid on the surface and migration of liquid by means of capillary flow and diffusion to surface increase with the temperature is shown in the Figure 4.23.

During our experiments we observed that the samples dried at $T=30^{\circ}\text{C}$ and 30%RH exhibit cracks. Likewise the samples dried at $T=80^{\circ}\text{C}$ and 90%RH exhibit cracks.

Therefore these two cases correspond to higher drying rates which lead to non-uniform and differential drying, induce structural and residual stresses which cause defects, such as cracking, bending and other deformations, which make the articles useless during the drying process.

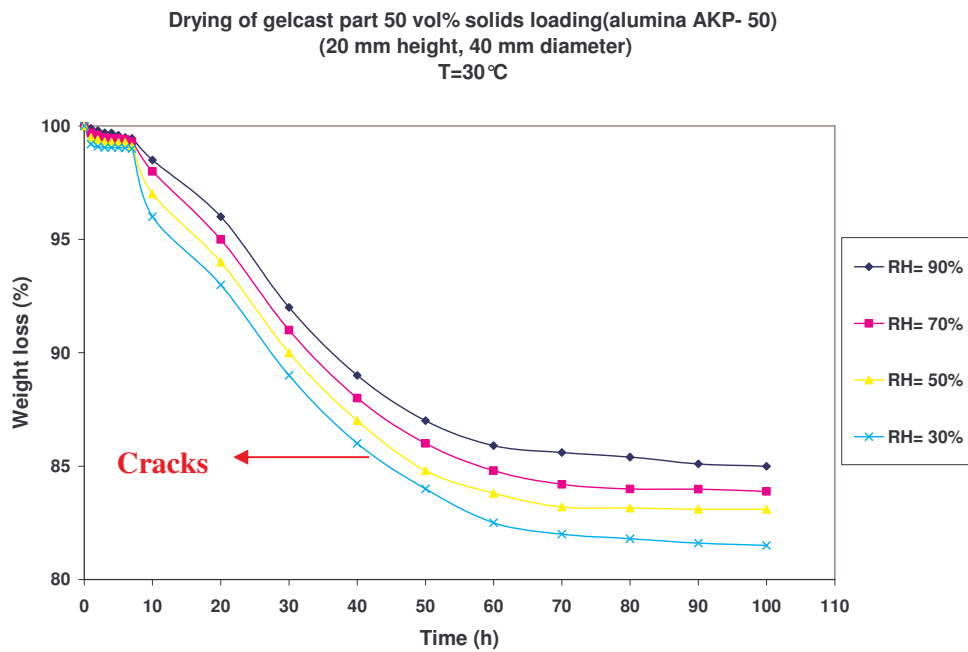


Fig. 4.22: Drying of gelcast part 50 vol% solids loading (alumina AKP-50) (20 mm height, 40 mm diameter) under constant temperature ($T=30^{\circ}\text{C}$) and changing humidity.

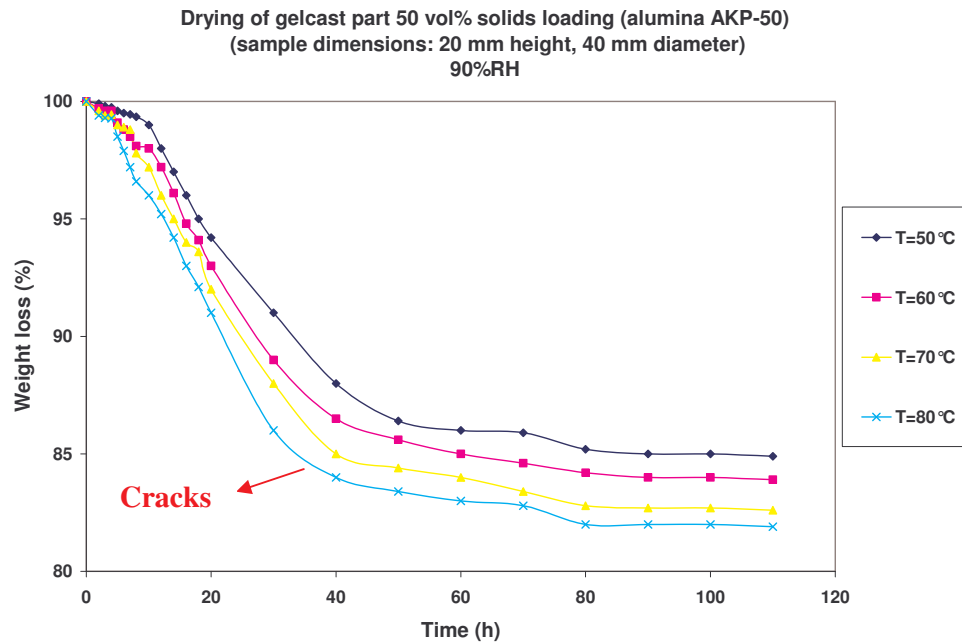


Fig. 4.23: Drying of gelcast part 50 vol% solids loading (alumina AKP-50) (20 mm height, 40 mm diameter) under constant humidity (90%RH) and changing temperature.

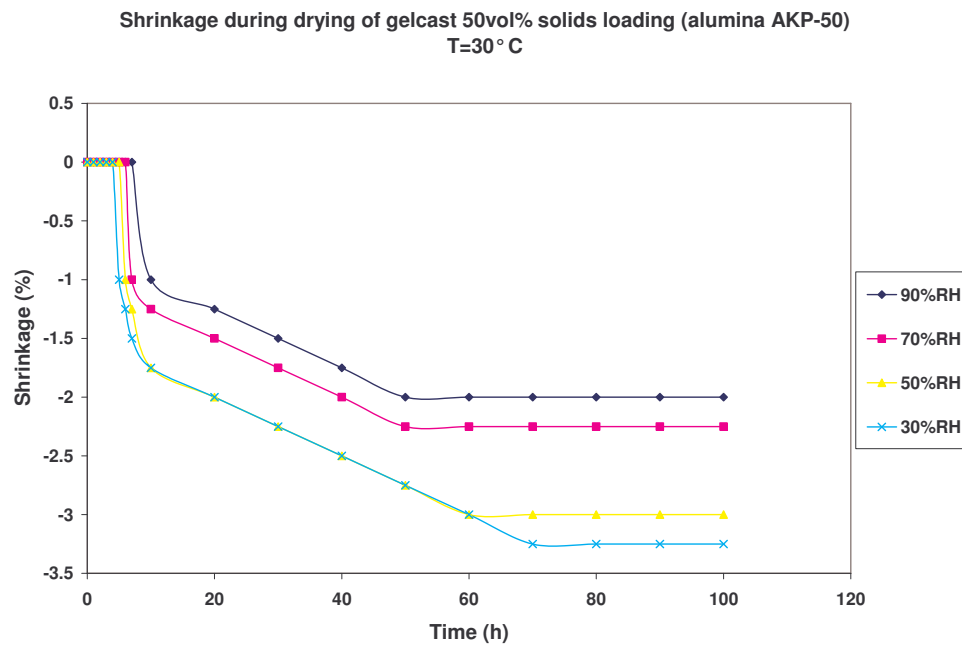


Fig. 4.24: Linear shrinkage during drying of gelcast part 50 vol% (alumina AKP-50) dried at different humidity.

However, to avoid any differential drying, drying has to be carried out under well-controlled temperature ($T < 80$) and humidity ($RH > 30\%$) conditions as shown in Figure 4.22 and Figure 4.23. As can be seen, the critical part of the drying cycle is limited to the removal of 25-30% of water. From there on the humidity can be lowered from 90% to 30% and the temperature can be raised from 30°C or 40°C to 80°C to obtain a constant rate of drying as shown in Figure 4.25. In this way the total drying time can be reduced to one third of the time needed under constant condition. In this way a 20 mm height X 40 mm diameter gelcast part have been dried without cracking.

The linear shrinkage during drying is 3.4 %, and volumetric shrinkage is 7.3%. The green density of the cast part is calculated to be 61% of theoretical density. Figure 4.26 shows the SEM micrograph of green alumina gelcast sample in which close packing of alumina particles is observed.

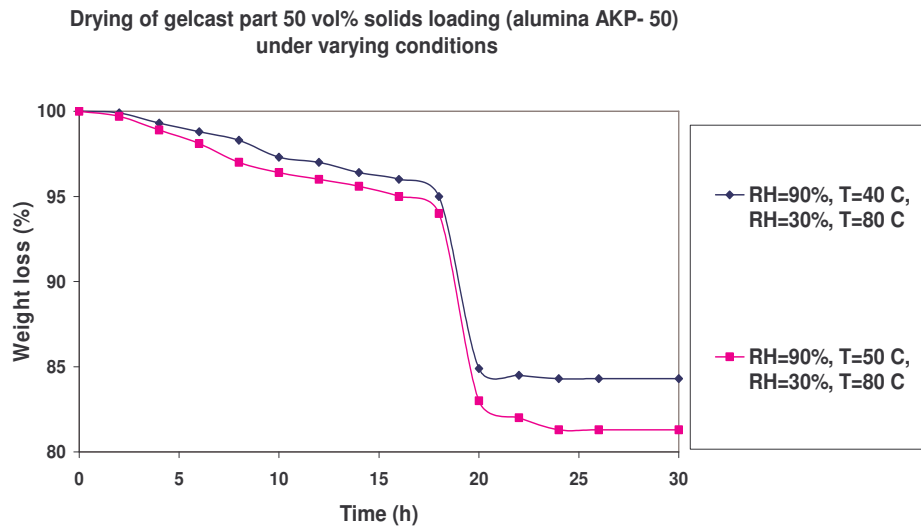


Fig. 4.25: Drying of gelcast part 50 vol% solids loading (alumina AKP-50) (20 mm height, 40 mm diameter) under varying conditions.

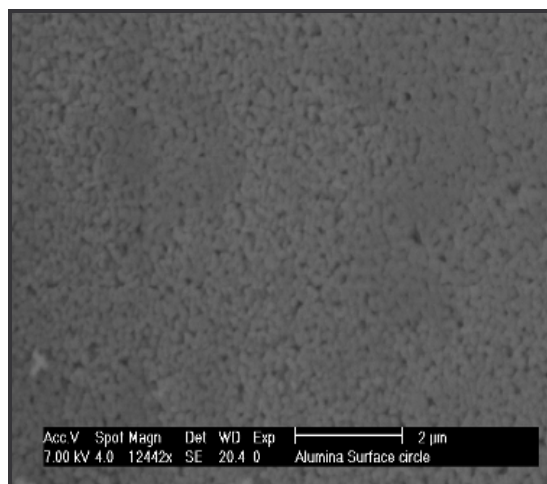


Fig. 4.26: SEM microstructure of green gelcast part 60 vol% (alumina AKP-50).

4.5.1 Properties of green alumina gelcast and alumina pressed in the green State.

The properties (pore size, porosity and green density) of gelcast and pressed samples are listed in Table 4.3, Table 4.4 and Table 4.5. From these tables we can observe that the samples 1-12 (Table 4.3) have a mean pore size of 2.3 μm , samples 20-25 (Table 4.5) have a mean pore size of 0.025 μm and samples have a mean pore size of 0.03. The gelcast bodies with PVP and antifoam n-octanol (Table 4.4) show narrower mean pore size compared to the gelcast bodies without PVP (Table 4.3), which also affect microstructure and density. The results obtained with these defoaming agents regarding the green density and fired density are in Table 4.4 and 4.7. The best results were obtained with n-octanol enhanced by the addition of polyvinyl pyrrolidone (PVP) with green density of 57.8% T.D (2.3) whereas we obtained densities of 46.9% T.D (1.87) and 46.7% T.D (1.86) for tributyl phosphate and silicone oil respectively as shown in Table 4.4.

The alumina pressed samples have the mean pore size approximately the same as for gelcasts with PVP and n-octanol antifoam.

The improvement in green density of gelcasts with PVP and n-octanol antifoam compared to gelcasts without PVP can be ascribed to a decrease of bubble-related pores in the materials.

The antifoam n-octanol is effective compare to tributyl phosphate and silicone oil. The results obtained with these defoaming agents regarding the green density and fired density are in Table 4.4 and 4.7. The best results were obtained with n-octanol enhanced by the addition of polyvinyl pyrrolidone (PVP) with green density of 57.8% T.D (2.3) whereas 46.9% T.D (1.87) and 46.7% T.D (1.86) for tributyl phosphate and silicone oil respectively as shown in Table 4.3. Thus n-octanol aids in the removal of air bubbles in the slurry during the deairing process. Bubbles entrapped in slurry and that could not be removed by the deairing process leave pores in the gelcast that act as defects and impair the properties of the materials. During the polymerization of HEMA monomers, a complicated polymer network is likely to be formed in the monomer solution with PVP through hydrogen bonds between PVP and PHEMA, resulting in an intimate mix of polymer chains. The monomer-polymer system with such a type of complicated polymer network shows relatively higher green density in contrast to a pure monomer system.

Table 4.3: Density, porosity and mean pore size of green alumina gelcast.

No	Solids loading of Al ₂ O ₃ - Akp-50	Monomer/ crosslinker	Ratio	Green body		
				Density (g/cm ³)	Porosity (%)	Mean pore size (μm)
1	50	HEMA/ MBAM	4:1	1.82	51.38	2.41
2	60	HEMA/ MBAM	4:1	1.84	50.82	2.39
3	50	HEMA/ MBAM	6:1	1.83	51.1	2.4
4	60	HEMA/ MBAM	6:1	1.83	51.1	2.32
5	50	HEMA/ MBAM	4:1	1.86	50.27	2.39
6	60	HEMA/ MBAM	4:1	1.89	49.47	2.32
7	50	HEMA/ MBAM	6:1	1.85	50.54	2.56
8	60	HEMA/ MBAM	6:1	1.85	50.54	2.38
9	50	HEMA/ MBAM	4:1	1.87	50.01	2.54
10	60	HEMA/ MBAM	4:1	1.89	49.47	2.56
11	50	HEMA/ MBAM	6:1	1.88	49.74	2.34
12	60	HEMA/ MBAM	6:1	1.89	49.47	2.32

Table 4.4: Density, porosity and mean pore size of green alumina gelcast.

No	Solid loading of Al ₂ O ₃ - Akp-50	Monomer/ crosslinker	Ratio	PVP Wt%	Green body		
					Density (g/cm ³)	Porosity (%)	Mean pore size (μm)
20	50	HEMA/ MBAM	4:1	2	2.24	42.49	0.03
21	60	HEMA/ MBAM	4:1	2	2.25	42.7	0.029
22	50	HEMA/ MBAM	4:1	4	2.27	42.31	0.0265
23	60	HEMA/ MBAM	4:1	4	2.29	42.5	0.024
24	50	HEMA/ MBAM	4:1	6	2.30	42.31	0.024
25	60	HEMA/ MBAM	4:1	6	2.33	41.98	0.0236

Table 4.5: Density, porosity and mean pore size of green alumina pressed.

No	Dry pressed alumina	Binder	plasticizer	% organic	Green Body		
					Density (g/cm ³)	Porosity (%)	Mean pore size (μm)
30	Pressed 50 MPa	Polyvinyl alcohol (3wt%)	Polyethylene glycol (1.5wt%)	4.5	2.1	40.46	0.031
31	Pressed 75 MPa	Polyvinyl alcohol (3wt%)	Polyethylene glycol (1.5 wt%)	4.5	2.18	39.10	0.03
32	Pressed 100MPa	Polyvinyl alcohol (3wt%)	Polyethylene glycol (1.5 wt%)	4.5	2.21	38.14	0.028

Green density of gelcast samples

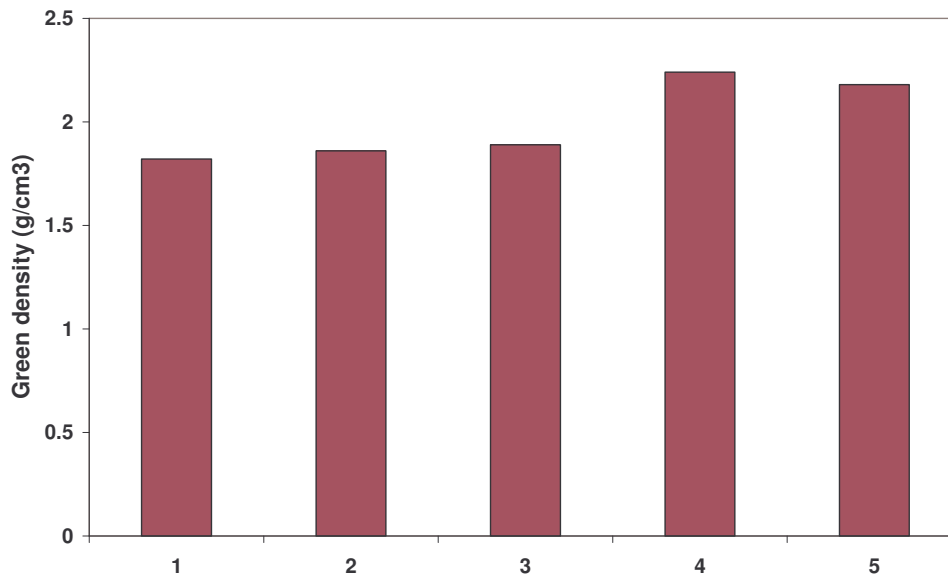


Fig. 4.27: Green densities of gelcasts with different antifoaming agents(contant :solid loading) : (1) with tributyl phosphate, (2) with silicone oil, (3) n-octanol, (4) with n-octanol and PVP, (5) pressed alumina 100 MPa.

4.6 Thermal gravimetric analysis

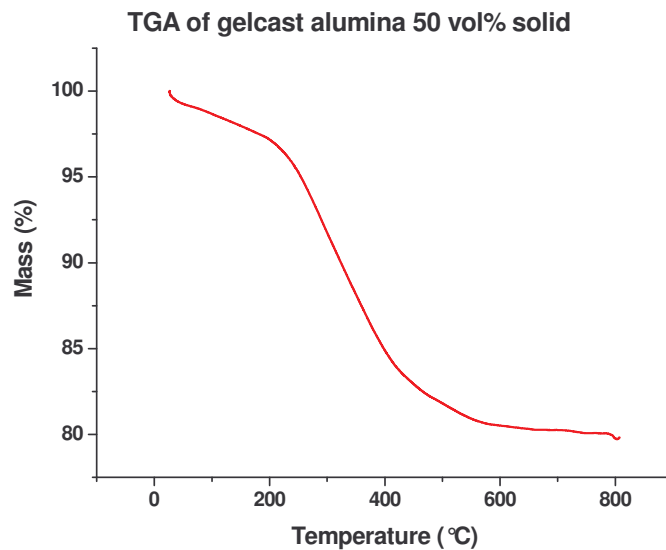


Fig. 4.28: TGA plot of gelcast 50vol% alumina AKP-50 (sample 1) at heating rate of 10°C/min in air.

Figure 4.28 is the TGA plot of the gelcast sample. TGA analysis showed with loss of 19.4% in the dried gelcast sample. More than 84% of the organic present in the gelcast sample was removed at temperature below 400°C. Therefore, a slow heating rate of 30°C/h must be used in this temperature range to avoid crack and deformation.

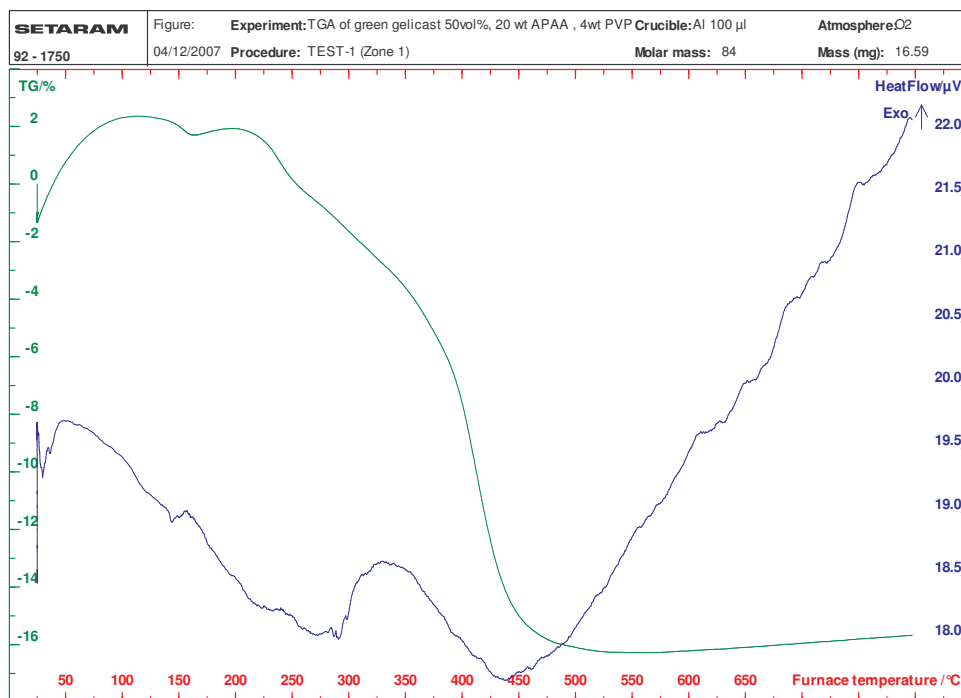


Fig. 4.29: TGA plot of alumina-cBN gelcast 50vol% (alumina AKP-50-cBN for a 9:1 volume ratio of Al_2O_3 and cBN) at heating rate of $10^\circ\text{C}/\text{min}$ in argon atmosphere.

Figure 4.29 is the TGA plot of the gelcast composite sample. TGA analysis showed with loss of 19.5% in the dried gelcast sample. Below 100°C it can be residual moisture. More than 95% of the organic present in the gelcast composite sample was removed at temperature below 450°C . Therefore, a slow heating rate of $30^\circ\text{C}/\text{h}$ must be used in this temperature range to avoid crack and deformation.

4.7 Binder burnout and Presintering

After drying, the parts were further processed in the conventional way. The total organic (monomer, crosslinker, dispersant, plastisizer) content is only approximately 19.5% wt.%. The binder was removed in a separate step or carried out immediately in the sintering furnace. The debinding profile applied was:

Room temperature to 100°C at 10°C/min,
 100°C to 400°C at 0.5°C/min,
 400°C to 900°C at 5°C/min, dwell at 900°C for 60 min,
 900°C to 25°C at 10°C/min.

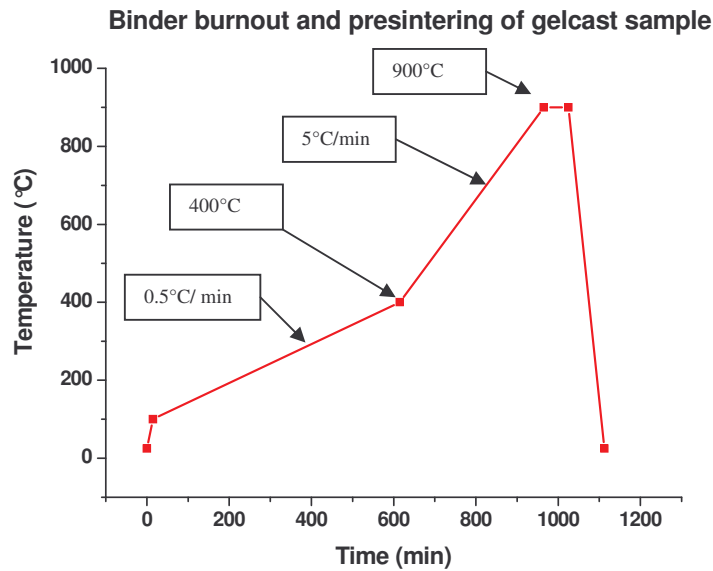


Fig. 4.30: Binder burnout and presintering profile plot for a gelcast sample.

After presintering the green density of the sample was determined by Archimedes method.

4.8 Sintering

The Sintering atmosphere was air for alumina gelcast and argon for alumina-cBN gelcast. Figure 4.31 shows the sintering profile plot.

The sintering profile used was:

Room temperature to 100°C at 10°C/min,

100°C to 400°C at 0.5°C/min,
400°C to 600°C at 5°C/min,
600°C to 1450°C at 10°C/min, dwell at 1450°C for 180 min,
1450°C to 25°C at 10°C/min.

The closer particle packing leads to sintering at lower temperatures and early densification. The sintered density of the cast at 1450°C is found to be 3.93 g cm^{-3} (98.7% of theoretical value) and vicker's microhardness by indentation was 2100 using a load of 2 kg. The shrinkage after sintering is 14%. Figure 4.32a and 4.32b is the SEM of the sintered sample, and showed uniformly distributed, fine microstructure $\sim 2\mu\text{m}$ grain size.

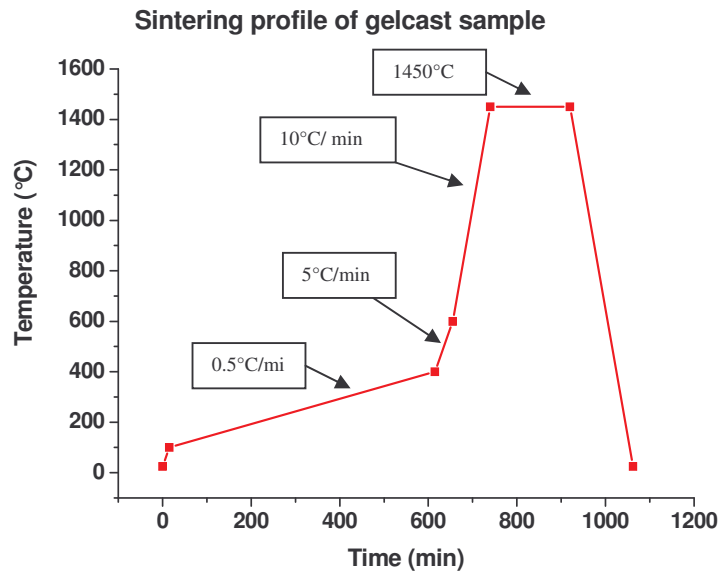


Fig. 4.31: Sintering profile plot for gelcast sample.

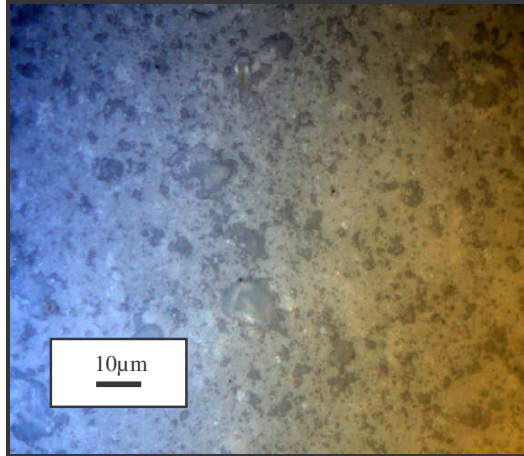


Fig. 4.32a: Microscopic image of sintered alumina gelcast (sample No 21).

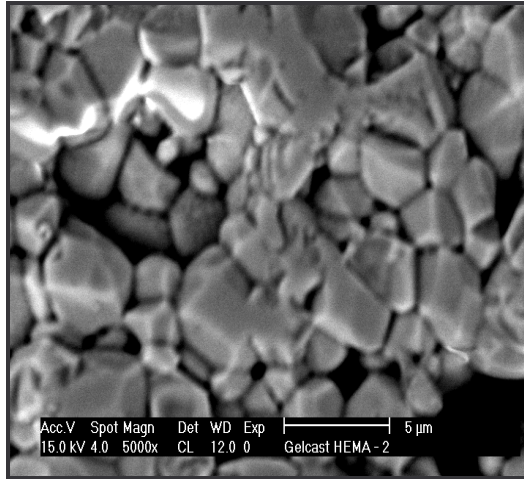


Fig. 4.32b: SEM micrograph of sintered alumina gelcast (sample No 21).

4.8.1 Densities and porosities of sintered alumina gelcast samples and alumina pressed samples

Densities and porosities of sintered gelcast samples are listed in Table 4.6 and 4.7, for alumina pressed samples there are listed in Table 4.8. From these table we observe that the densities of the gelcast 50vol% (sample 1) is 3.37 (84.6%T.D) less than 3.82 (85.9%T.D) for the gelcast 60vol% (sample 2). We observe that fired density is higher for gelcast with higher green density. As one would expect, increasing solids loading results in less shrinkage and a higher density. Although gelcasting results in a slightly greater shrinkage (14%) than die pressing (13%),

higher density value was also obtained, thus, a more uniform structure is observed in Figure 4.33 than in Figure 4.34. No obvious density difference between different sections of gelcast body has been observed. Moreover, based on our observation, no cracking has occurred. Study of their microstructures by inspecting the pore size distributions of two kinds of green bodies reveals that the gelcast sample has a smaller median pore size than the die pressed sample, which is indicative of a more homogeneous microstructure. The results in Figure 4.33 and table 4.7 are in good agreement with those from SEM examination and density measurement, suggesting that the homogeneously dispersed alumina particles in the suspension obtained by adding dispersant (APAA), monomer (HEMA), polymer (PVP), antifoam (n-octanol) and thoroughly milling were effectively conserved in the green body during in situ polymerization and then in the sintered samples.

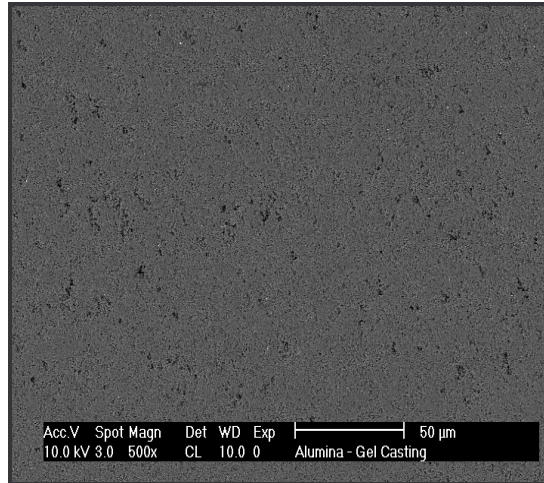


Fig. 4.33: SEM micrograph of polished sintered alumina gelcast 50 vol% solids loading (sample No 20).

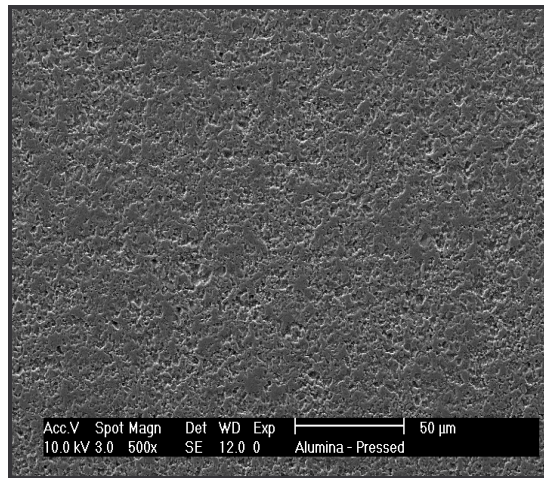


Fig. 4.34: SEM micrograph of polished sintered alumina pressed (sample No 30).

Table 4.6: Densities and porosities of sintered alumina gelcast samples.

No	Solid loading of Al ₂ O ₃ Akp-50	Monomer/ crosslinker	Ratio	Sintered Body		
				Density (g/cm ³)	Porosity (%)	Open porosity (%)
1	50	HEMA/ MBAM	4:1	84.6%TD	15.4	2.36
2	60	HEMA/ MBAM	4:1	85.9.%TD	14.1	2.40
3	50	HEMA/ MBAM	6:1	84%TD	16	2.34
4	60	HEMA/ MBAM	6:1	84.82%TD	15.18	2.36
5	50	HEMA/ MBAM	4:1	88.6%TD	11.4	2.47
6	60	HEMA/ MBAM	4:1	89.38%TD	10.62	2.49
7	50	HEMA/ MBAM	6:1	87.1%TD	12.9	2.43
8	60	HEMA/ MBAM	6:1	87.8%TD	12.2	2.45
9	50	HEMA/ MBAM	4:1	88.6%TD	11.4	2.49
10	60	HEMA/ MBAM	4:1	89.01%TD	10.99	2.48
11	50	HEMA/ MBAM	6:1	87.03%TD	12.97	2.43
12	60	HEMA/ MBAM	6:1	88.3%TD	11.7	2.46

Table 4.7: Densities and porosities of sintered alumina gelcast samples with n-octanol and PVP.

No	Solid loading	Monomer / crosslinker	Ratio	PVP	Sintered Body	
					Density (g/cm ³)	Porosity (%)
20	50	HEMA/MBAM	4:1	2	3.83 (96.13%TD)	4.9
21	60	HEMA/MBAM	4:1	2	3.85 (96.85%TD)	4.2
22	50	HEMA/MBAM	4:1	4	3.88 (97.48%TD)	2.8
23	60	HEMA/MBAM	4:1	4	3.89 (97.64%TD)	2.7
24	50	HEMA/MBAM	4:1	6:1	3.88 (97.56%TD)	2.5
25	60	HEMA/MBAM	4:1	6:1	3.93 (98.68%TD)	1.4

Table 4.8: Densities and porosities of sintered pressed alumina samples.

No	Dry pressed alumina	Binder	plasticizer	% organic	Sintered Body	
					Density (g/cm ³)	Porosity (%)
30	Pressed 50 MPa	Polyvinyl alcohol (3wt%)	Polyethylene glycol (1.5wt%)	4.5	3.78 (95.04%TD)	4.96
31	Pressed 75 MPa	Polyvinyl alcohol (3wt%)	Polyethylene glycol (1.5 wt%)	4.5	3.8 (96.26%TD)	3.8
32	Pressed 100MPa	Polyvinyl alcohol (3wt%)	Polyethylene glycol (1.5 wt%)	4.5	3.8 (97.42%TD)	2.6

4.8.2 Sintering of Alumina-cBN gelcast (volume ratio of Al_2O_3 : cBN of 9:1)

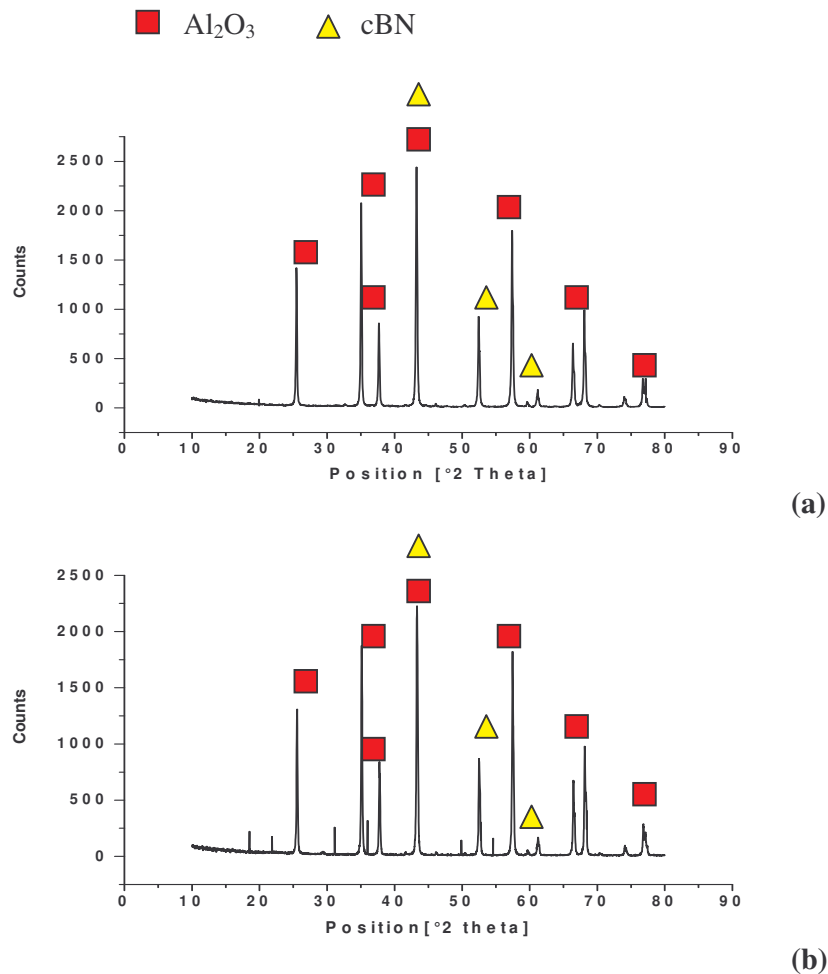


Fig. 4.35: XRD analysis of alumina-cBN gelcast (volume ratio of Al_2O_3 : cBN 9:1) before sintering (a), alumina-cBN gelcast sintered at 1450°C in argon (b)

Figure 4.35 shows the XRD patterns of Alumina-cBN gelcast before firing, and fired at 1450°C in argon. The gelcast was fired in air to examine to which extent is the cBN phase lost when firing under these conditions. When the gelcast is fired in argon atmosphere, we observe that XRD pattern is the same as for the green

gelcast. But when fired in air, cBN is reacting with oxygen to form Aluminium-Borate. Cracks were found in the samples after firing as it can be seen in Figure 4.37. It is worth noting that incorporation of cBN resulted in lower densities compared to alumina on its own. Furthermore there isn't much change in density of the material with 10 vol% cBN with increase in sintering time as is the case with alumina. The fired shrinkage was around 3% contrary to alumina gelcast that has 14%. This can be attributed to the high resistance of cBN to plastic deformation under the sintering conditions employed.



Fig. 4.36: Photographic image of alumina-cBN gelcasts sintered in argon at 1450°C for 3 hours.



Fig. 4.37: Photographic image of alumina-cBN gelcasts sintered in air at 1450°C for 3 hours.

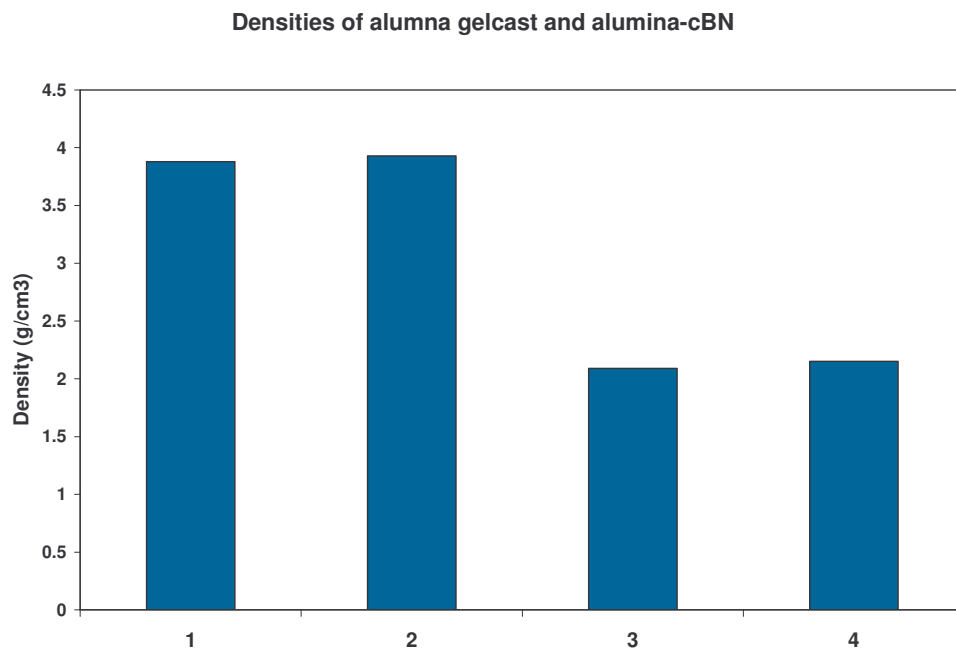


Fig. 4.38: Comparison of densities of alumina gelcast with alumina-cBN(10 vol%) gelcast sintered at 1450°C in air and argon respectively (1): Alumina gelcast 50vol%, (2) Alumina gelcast 60vol%, (3) Alumina-cBN 50 vol%, (4) Alumina-cBN 60 vol%.

Table 4.9: Densities and linear shrinkage of alumina-cBN samples

No	Composition	Green Density (g/cm ³)	Shrinkage (%)	Sintered density (g/cm ³)	Shrinkage (%)
40	Al ₂ O ₃ -cBN 50vol% n-octanol	1.55	0.60	1.9	1.70
41	Al ₂ O ₃ -cBN 60vol% n-octanol-PVP	1.68	0.42	2.1	1.66
42	Al ₂ O ₃ -cBN 50vol% n-octanol	1.79	0.56	2.09	1.46
43	Al ₂ O ₃ -cBN 60vol% n-octanol-PVP	1.82	0.54	2.14	1.22

Incorporation of 10% cBN as a second phase resulted in a very porous microstructure as it can be seen from the Figure 4.39 and that is confirmed by the figures of green densities given in Table 4.9. Therefore the green density of Al_2O_3 -cBN gelcast is low compare to the Al_2O_3 gelcast this is not the case for their fired densities.

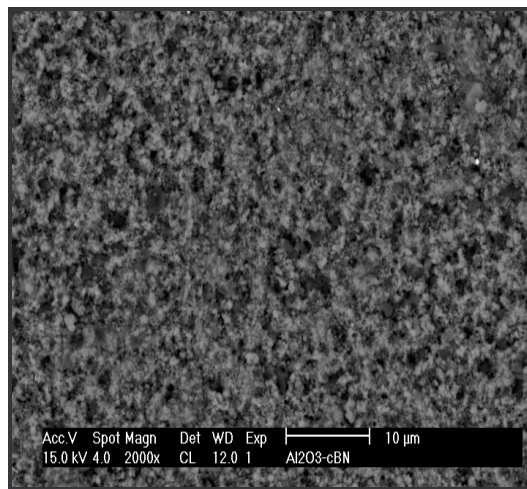


Fig. 4.39: SEM of green Al_2O_3 -cBN gelcast (sample No 40).

4.9 Grinding and Polishing

The microscopic images gelcast sample at each step of the grinding and polishing process are shown. From Fig. 4.40 to Fig. 4.43 show surface after rough grinding(plane grinding), from Fig. 4.44 to Fig. 4.46 show surface after intermediate polishing(fine grinding) and from Fig. 4.47 to Fig. 4.50 show scratch-free surface after final polishing. Black spots are pores.

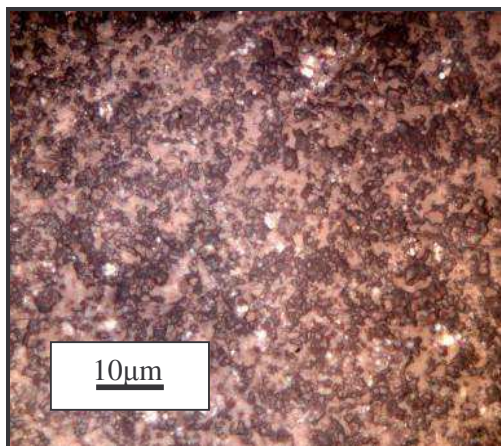


Fig. 4.40: Microscopic image of gelcast 50 vol.% HEMA(20wt%)-PVP(4wt%) before grinding.

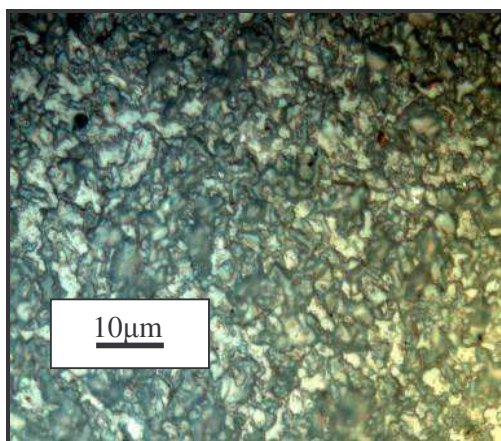


Fig. 4.41: Microscopic image of gelcast 50 vol.% HEMA(20wt%)-PVP(4wt%) after grinding for 30 min. with diamond disc # 220.

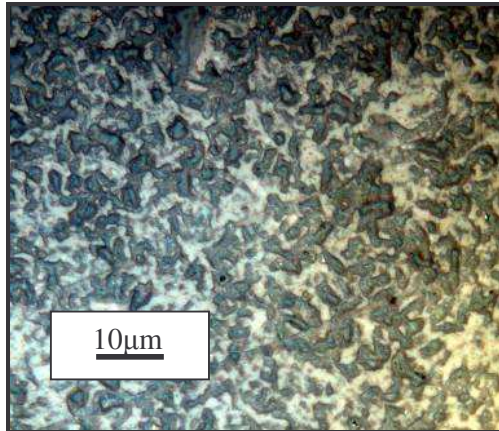


Fig. 4.42: Microscopic image of gelcast 50 vol.% HEMA(20wt%)-PVP(4wt%) after grinding for 60 min with diamond disc # 220 and 30 min with diamond disc #600.

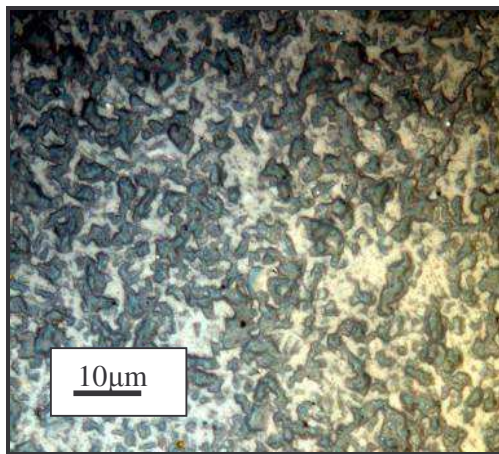


Fig. 4.43: Microscopic image of gelcast 50 vol.% HEMA(20wt%)-PVP(4wt%) after grinding for 60 min (#220), 30 min (#600) and 30 min (#1200).

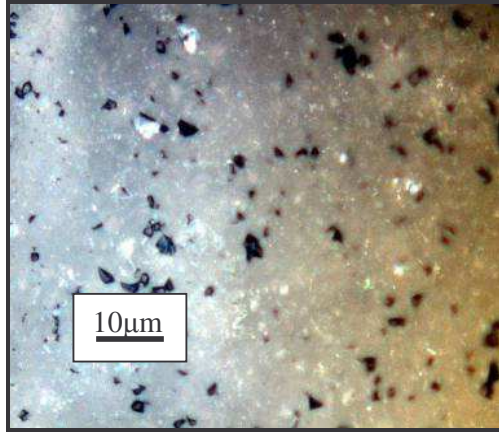


Fig. 4.44: Microscopic image of gelcast 50 vol.% HEMA(20wt%)-PVP(4wt%) after grinding for 60 min (#220), 30 min (#600), 15 min (#1200), polishing with diamond suspension for 5 min.

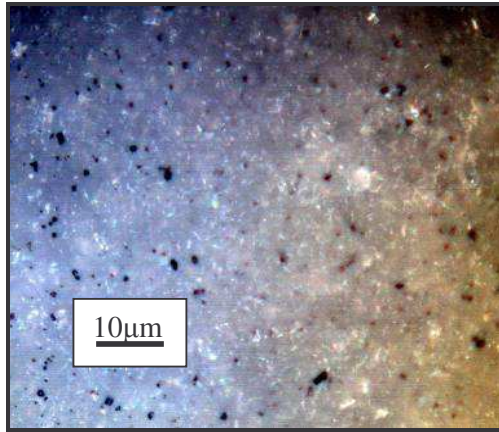


Fig. 4.45: Microscopic image of gelcast 50 vol.% HEMA(20wt%)-PVP(4wt%) after grinding for 60 min (#220), 30 min (#600) , 30 min (#1200), polishing with diamond suspension for 15 min.

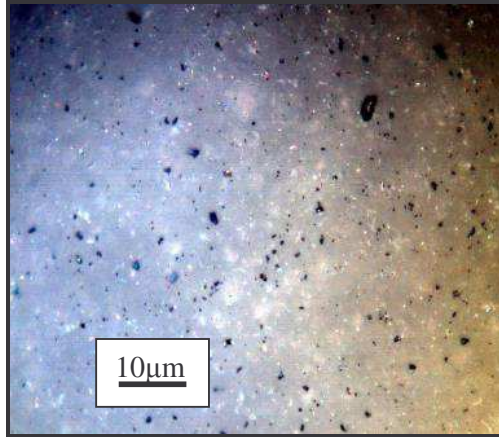


Fig. 4.46: Microscopic image of gelcast 50 vol.% HEMA(20wt%)-PVP(4wt%) after grinding for 60 min (#220), 30 min (#600) , 30 min (#1200), polishing with diamond suspension for 25 min.

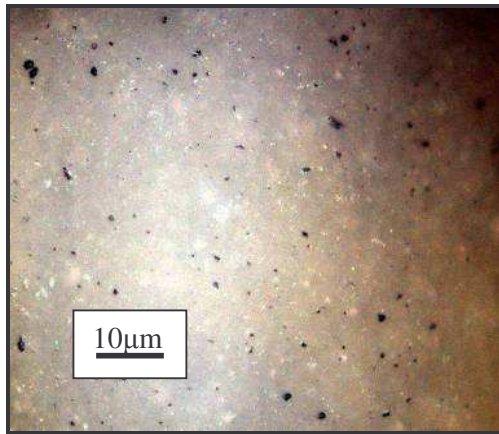


Fig. 4.47: Microscopic image of gelcast 50 vol.% HEMA(20wt%)-PVP(4wt%) after grinding for 60 min (#220), 30 min (#600), 30 min (#1200), polishing with diamond suspension for 35 min.

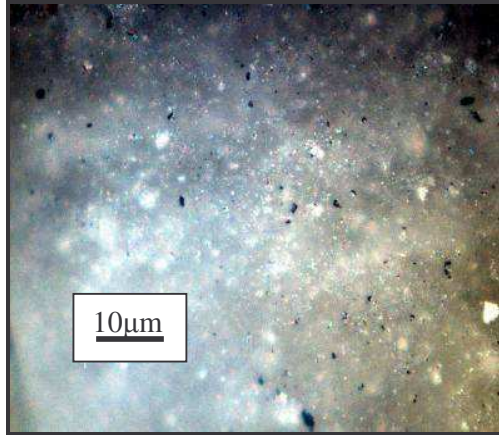


Fig. 4.48: Microscopic image of gelcast 50 vol.% HEMA(20wt%)-PVP(4wt%) after grinding for 60 min (#220), 30 min (#600), 30 min (#1200), polishing with diamond suspension for 45 min.

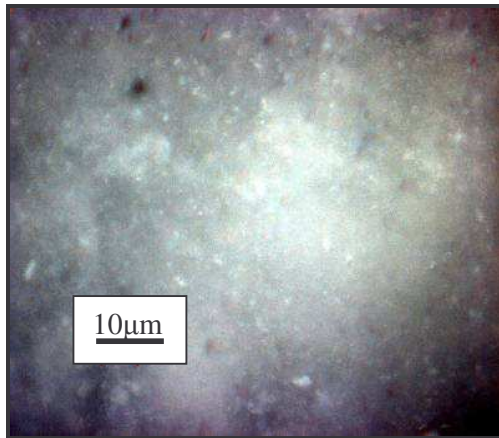


Fig. 4.49: Microscopic image of gelcast 50 vol.% HEMA(20wt%)-PVP(4wt%) after grinding for 60 min (#220), 30 min (#600), 30 min (#1200), polishing with diamond suspension for 55 min.

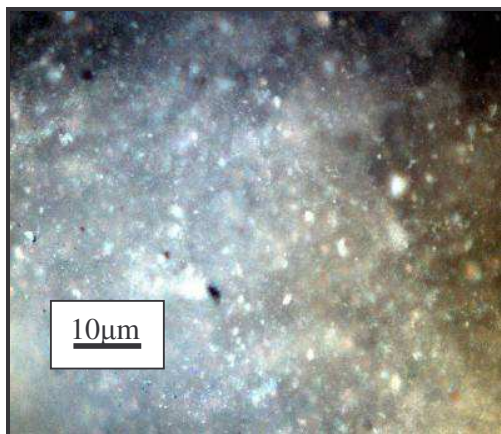


Fig. 4.50: Microscopic image of gelcast 50 vol. % HEMA(20wt%)-PVP(4wt%) after grinding for 60 min (#220), 30 min (#600) , 30 min (#1200), polishing with diamond suspension for 65 min.

CHAPTER 5 CONCLUSIONS

The followings are the conclusions drawn based on this investigation:

(1) Gelcasting of alumina and alumina-cBN(10vol%) powder has been investigated. The gelcasting process conditions were optimized based on investigation of the basic processes involved, including the suspension parameters, drying behaviour, debinding conditions, and sintering process. The optimum concentration of the dispersing agent ammonium poly(acrylic acid) was found to be 1wt%. This dispersant concentration corresponds to the lowest value of viscosity. It was found that the alumina slurry and the alumina-cBN exhibit respectively at pH=8, pH=6 (pH=10) high absolute values of zeta potential, suspensions prepared within this region are colloidally stable. The optimal suspension conditions for the preparation of gelcast part were found as follows: 1 wt% dispersant (APAA), 60 vol% solid, 5 wt% monomer(HEMA), 4.5wt% PVP, pH=8 (alumina) and pH=10 (alumina-cBN).

Alumina powders of high specific area and high solid loadings lead to high bubble content both in as-prepared and deaired slurries. Deairing under vacuum with addition of antifoaming agent to aid deairing is important for the elimination of bubbles entrapped during mixing/milling operation. N-octanol was found to be the most effective antifoaming agent for alumina slurry used in this work.

Drying was carried under temperature and humidity control. It was found that drying process has to be conducted in two stages : first at high humidity (90%RH) and low temperature (40°C) in the first hours, this is necessary to avoid cracks of the part. The second stage of the process starts when 25-30% of water content has been removed. From there on the temperature can be raised to 80-100°C and the humidity can be lowered to 30% RH this speeding the drying process. In this way the total drying time can be reduced to one third of the total time needed under constant conditions. The wet body shrank by 2-3% upon drying in a humidity-controlled chamber. It was clear that the slurry was well dispersed as it can also be

shown by SEM observation of the microstructure of the green body and a high sintered density can be achieved.

(2) The addition of PVP greatly increased the homogeneity of the microstructure and contributed to the increase of density of the green gelcast from HEMA premix solution. The green gelcast body 60vol% with a green density of 1.89g/cm^3 (47.5%T.D) has been increased to 2.33 g/cm^3 (58.5% T.D) with an addition of 4 wt% PVP in the premix. The green gelcast body can be thermally debinded by employing appropriate heating rate of 0.5°C/min from ambient temperature to 450°C .

(3) A fired density of 3.93g/cm^3 (98.7%T.D) was achieved for alumina gelcast sintered at 1450°C for 3 hours, with 13-14% shrinkage. This density was higher than the density of pressed alumina (97.4%T.D) sintered at the same conditions. The microstructure of gelcasts was more homogeneous than that of pressed samples, this is particularly realized by controlling and manipulating the forces between the particles in suspension in a liquid (colloidal processing).

(4) Incorporation of cBN resulted in low green density of the gelcast and porous microstructure. Sintering under argon at 1450°C for 3 hours resulted in lower fired density (density of alumina-cBN gelcast 60 vol% = 2.14) than the alumina (density of alumina gelcast 60 vol% = 3.93g/cm^3) on its own. Therefore densification has to be improve by increasing either sintering temperature or pressure.

(5) These results demonstrate that gelcasting is a viable technique for the sintering of alumina in various complex shapes with high density. High solids loading green bodies with uniform structure were produced by gelcasting. For synthesis of alumina-cBN further investigations are necessary to optimize the green body structure and especially the sintering process for the densification of $\text{Al}_2\text{O}_3/\text{cBN}$ composite.

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