

GELCASTING OF ALUMINA CERAMICS WITH
GELATIN AND CARRAGEENAN GUM AND
INVESTIGATION OF THEIR MECHANICAL
PROPERTIES

A thesis Submitted to
the Graduate School of Engineering and Sciences of
İzmir Institute of Technology
in Partial Fulfillment of The Requirements for the Degree of

MASTER OF SCIENCE

in Materials Science and Engineering

by
Galip Sarper KOÇLAR

February, 2013

İZMİR

We approve the thesis of **Galip Sarper KOÇLAR**

Examining Committee Members:

Prof. Dr. Muhsin ÇİFTÇİOĞLU

Department of Chemical Engineering, İzmir Institute of Technology

Prof. Dr. Devrim BALKÖSE

Department of Chemical Engineering, İzmir Institute of Technology

Assist. Prof. Dr. Özgeç EBİL

Department of Chemical Engineering, İzmir Institute of Technology

20 February 2013

Prof. Dr. Muhsin ÇİFTÇİOĞLU

Supervisor, Department of Chemical Engineering
İzmir Institute of Technology

Assoc. Prof. Dr. Mustafa M. DEMİR

Head of the Department of
Materials Science and Engineering

Prof. Dr. R. Tuğrul SENCER

Dean of the Graduate School
of Engineering and Sciences

ACKNOWLEDGEMENTS

In first turn, I'd like to thank to my advisor Prof. Dr. Muhsin Çiftçiođlu because of his advices and valuable contributions to my thesis. I'd like to thank Specialist Deniz ŐimŐek, Dr. Ali Emrah Çetin because of their great helps to my experimental study. I specially thank to my friend Dr. Erdem Őahin because of his friendship and kindness. Finally, I'd like to express my gratitude to my parents because of their emotional and economical supports.

ABSTRACT

GELCASTING OF ALUMINA CERAMICS WITH GELATIN AND CARRAGEENAN GUM AND INVESTIGATION OF THEIR MECHANICAL PROPERTIES

In this study, use of gelatin and carrageenan gum as gel formers in gelcasting process of alumina ceramics was aimed. The effects of each gel former on the mechanical properties of gelcasted alumina ceramics were distinctly investigated.

Firstly, an experimental design was made according to pre-experimental studies and researches. In this experimental design, it was determined what the factors should be and how the levels of factors should change. Two groups of gelcasting slips were prepared with alumina powder. One of them was the group that contained gelatin with changing ratios from 3 to 6 wt%. Other was the group that contained carrageenan gum with changing ratios from 1 to 2 wt%. Alumina powder amounts of the slips in also each group were the same and changing from 47 to 53 vol%. Furthermore, in order to see the direct effect of each gel former type and amount on mechanical properties and compare the methods of gelcasting and slip casting, alumina slips that contained no gelatin or carrageenan gum were also prepared.

Green alumina samples in suitable shapes for mechanical tests were obtained by gelcasting method from the prepared slips. After green samples were dried, half of them were sintered at 1550 °C. Rest of them weren't subjected to any heat treatment. Green samples in block shape were cut in suitable dimensions for 3-point bending test before they were sintered. Shrinkage and densification ratios of the alumina samples after drying and sintering were measured and calculated.

At the end of the mechanical tests applied on green and sintered alumina ceramics, data about change in their bending strength, compressive strength and hardness values due to varying gel amount and sintering were obtained. These data were analyzed, then the obtained results were interpreted. While optimum gel former amount needed for maximum compressive and bending strength of gelatin-gelcasted alumina samples was 5 wt%., this amount for that of gum-gelcasted alumina samples was 1.7 wt%. The effect of alumina solid loading on mechanical properties of gelcasted alumina samples was unclear. After sintering of gelatin-gelcasted alumina samples, the densification reached to a maximum of 95.80%.

ÖZET

ALUMİNA SERAMİKLERİN JELATİN VE KARAJENAN GUM İLE JEL DÖKÜMÜ VE MEKANİK ÖZELLİKLERİNİN ARAŞTIRILMASI

Bu çalışmada jelatin ve karajenan gumın bir jel sistemi olarak alumina seramiklerin jel döküm işleminde kullanılması amaçlanmıştır. Her bir jelin ayrı ayrı jel dökülmüş alumina seramiklerin mekanik özelliklerine etkisi incelenmiştir.

İlk olarak, önceden yapılan deneysel çalışmalar ve araştırmalara dayanılarak bir deneysel dizayn yapılmıştır. Bu deneysel dizaynda faktörlerin ne olması gerektiği, faktörlerin levellerinin nasıl değişmesi gerektiği belirtilmiştir. Bu doğrultuda alumina tozundan iki grup jel-döküm çamuru hazırlandı. Bu gruplardan biri içinde ağırlıkça %3'ten %6' e kadar değişen oranlarda jelatin bulunduran gruptur. Diğer grup ise içinde ağırlıkça %1'den %2'ye kadar carragenan gum bulunduran gruptur. İki grupta da bulunan jel-döküm çamurlarının alumina toz miktarları hacimce 47-53 aralığında değişmektedir. Ayrıca, herbir jelin mekanik özelliklere doğrudan etkisinin görülmesi ve jel döküm ile slip döküm yöntemlerinin karşılaştırılması için jelatin veya gum içermeyen döküm çamurları da hazırlandı.

Hazırlanan döküm çamurlarından jel döküm yöntemi ile mekanik testler için uygun boyutlarda ham alumina numuneler elde edildi. Numuneler kurutulduktan sonra numunelerin yarısı 1550 °C sıcaklıkta sinterlendi. Diğer yarısı herhangi bir ısıl işlemde geçirilmedi. Blok şeklindeki ham numuneler sinterlenmeden önce üçlü eğme testi için uygun boyutlarda kesildi. Numunelerin kuruma ve sinterleme sonrası boyutsal küçülmeleri ve densifikasyon oranları ölçüldü ve hesaplandı.

Ham ve sinterlenmiş alumina seramiklere uygulanan mekanik testler sonucunda seramiklerin eğilme mukavemeti, basma mukavemeti ve sertlik değerlerinin değişen jel miktarına ve sinterlemeye bağlı değişimleri hakkında veriler elde edildi. Bu veriler analiz edildi ve elde edilen sonuçlar yorumlandı. Jelatin ile jel dökülmüş alumina numunelerin en yüksek basma ve eğme mukavemetleri için gerekli optimum jel miktarı ağırlıkça %5 iken, bu miktar gum ile jel dökülmüş alumina numuneler için %1.7 idi. Alumina miktarının, jel dökülmüş alumina numunelerin mekanik özelliklerine etkisi net değildi. Jelatin ile jel dökülmüş alumina numuneler sinterlendikten sonra maksimum %95.82 densifikasyon değerine ulaşıldı.

TABLE OF CONTENTS

| | |
|---|------|
| LIST OF FIGURES..... | viii |
| LIST OF TABLES..... | xi |
| CHAPTER 1. INTRODUCTION | 1 |
| 1. 1. Traditional Gelcasting Process..... | 3 |
| 1. 1. Slip Preparation..... | 5 |
| 1. 2. Importance of Solid Loading | 7 |
| 1. 3. Traditional Gelcasting Molds..... | 8 |
| 1. 4. Binder Burn-out Process | 10 |
| 1. 5. Important Points at Traditional Gelcasting Process..... | 11 |
| 1. 2. Thermoreversible and Natural Gelcasting Systems..... | 11 |
| 2.1. Gelatin..... | 16 |
| 2. 2. Composition and Some Properties of Gelatin..... | 16 |
| 2. 3. Some Technical Uses of Gelatin..... | 17 |
| 2. 4. Carrageenan Gum..... | 17 |
| 1. 3. Some Applications of Alumina Ceramics..... | 19 |
| CHAPTER 2. EXPERIMENTAL PROCEDURE..... | 21 |
| 2. 1. Materials..... | 21 |
| 2. 2. Method..... | 21 |
| 2. 1. Rheometric Analysis..... | 21 |
| 2. 2. Experimental Design..... | 22 |
| 2. 3. Sample Preparation and Mechanical Tests..... | 23 |
| CHAPTER 3. RESULTS and DISCUSSION..... | 31 |
| 3. 1. Rheometric Analysis of Gelatin..... | 33 |
| 3. 2. Density Measurements of the Samples..... | 34 |
| 3. 3. Hardness Measurements of the Samples..... | 36 |
| 3. 4. Shrinkage Measurements of the Samples..... | 39 |
| 3. 5. Compressive Strength Measurements of the Samples..... | 40 |

| | |
|--|----|
| 3. 6. Three-point Bending Test of the Samples..... | 48 |
| CHAPTER 4. CONCLUSION | 51 |
| CHAPTER 5. REFERENCES..... | 53 |
| APPENDICES | |
| APPENDIX A. AMOUNTS OF THE MATERIALS USED IN GELCASTING SLIP PREPARATION..... | 56 |
| APPENDIX B. EXPERIMENTAL DATA OBTAINED FROM SOME MEASUREMENTS AND MECHANICAL TESTS..... | 57 |

LIST OF FIGURES

| <u>Figure</u> | <u>Page</u> |
|--|-------------|
| Figure 1. Ceramic parts with complex shapes produced by gelcasting method..... | 1 |
| Figure 2. Magnified schematic representation of a microscopic cross-section of wet and dried gelcast parts..... | 4 |
| Figure 3. Traditional gelcasting flow chart | 5 |
| Figure 4. Gelation mechanism in traditional gelcasting..... | 6 |
| Figure 5. Polymeric gelcasting mold and the corresponding gelcast product..... | 10 |
| Figure 6. Viscosity of 2-ethylhexanol (2EH) and thermoreversible gel with 17.5 wt% $A_{25}B_{116}A_{25}$ in 2EH as a function of temperature..... | 12 |
| Figure 7. Gelation mechanism of polysaccharides..... | 13 |
| Figure 8. Chemical structure of gelatin..... | 17 |
| Figure 9. Different types of carrageenans | 18 |
| Figure 10. Experiment flow chart..... | 24 |
| Figure 11. a) Plexiglass molds b) Pasteboard molds..... | 25 |
| Figure 12. a) Coin like green alumina samples. b) Cylindrical green alumina samples. c) Green alumina large blocks. d) Green alumina bars after cutting from the green alumina blocks..... | 26 |
| Figure 13. a) Green alumina test samples b) Sintered alumina test samples c) Sintered alumina test samples d) Alumina test samples are being prepared for density measurements..... | 28 |
| Figure 14. a, b) Making plaster molds. c, d) Plaster molds were dried and then alumina slip casted..... | 29 |
| Figure 15. XRD analysis result of the alumina powder..... | 31 |
| Figure 16. Particle size distribution of the alumina powder..... | 32 |
| Figure 17. TGA analysis of the alumina powder..... | 32 |
| Figure 18. Change in viscosity of gelatin solution due to its gelatin amount and temperature..... | 33 |
| Figure 19. Sintered alumina samples..... | 34 |
| Figure 20. Change in densification percentage due to gelatin and alumina amounts.... | 35 |
| Figure 21. Optical microscopy images of the gelcasted green alumina samples. The indents of diamond pyramid indenter are seen..... | 36 |

| | |
|---|----|
| Figure 22. The graph of change in hardness of green samples due to their gelatin and alumina amounts..... | 37 |
| Figure 23. The graph of change in hardness of green samples due to their carrageenan gum and alumina amounts..... | 38 |
| Figure 24. Comparison of gels used in alumina sample production regarding hardness..... | 39 |
| Figure 25. a) Green large alumina ceramics. b) Sintered small cubic alumina pieces..... | 40 |
| Figure 26. The graphs of change in compressive strength of green samples due to their gelatin and alumina amounts..... | 41 |
| Figure 27. The graphs of change in compressive strength of sintered samples due to their gelatin and alumina amounts..... | 41 |
| Figure 28. Stress-strain diagram of a green sample obtained as a result of compression test..... | 42 |
| Figure 29. Stress-strain diagram of two sintered alumina samples obtained as a result of compression test..... | 43 |
| Figure 30. The graphs of change in compressive strength of green samples due to their carrageenan gum and alumina amounts..... | 44 |
| Figure 31. The graphs of change in compressive strength of sintered samples due to their carrageenan gum and alumina amounts..... | 44 |
| Figure 32. Stress-strain diagram of two sintered alumina samples obtained as a result of compression test..... | 45 |
| Figure 33. Comparison of gels' effects on green alumina samples regarding compressive strength | 46 |
| Figure 34. Comparison of gels' effects on sintered alumina samples regarding compressive strength..... | 47 |
| Figure 35. The graphs of change in bending strength of green alumina samples due to their gelatin amounts..... | 48 |
| Figure 36. The graphs of change in bending strength of sintered alumina samples due to their gelatin amounts..... | 49 |

LIST OF TABLES

| <u>Table</u> | <u>Page</u> |
|--|--------------------|
| Table 1. Mechanical properties of 99.5% alumina..... | 19 |
| Table 2: Design of experiment table for the experiment..... | 23 |
| Table 3: Densification percentages of the samples after sintering at 1600 °C..... | 34 |
| Table 4: Vickers hardness number values of the gelatin-gelcast green alumina samples..... | 36 |

CHAPTER I

INTRODUCTION

Gelcasting is a ceramic forming process which is used for the production of complex shaped mechanically strong inorganic materials with high density by incorporating ceramic particles into a flowable sol which can form a gel. It was developed at Oak Ridge National Laboratory by Ogbemi O. Omatete and his colleagues in 1991. The process involves the preparation of a suspension by using a ceramic powder and a water based monomer solution which is further poured into a mold. The slurry is then polymerized by adding an initiator. After gelled part is rejected from the mold, the polymer-organic phase of the solidified gel is thermally removed. The remaining inorganic is finally sintered to form a ceramic body [1-6].

Application of gelcasting method is not limited to a specific ceramic powder. Almost insignificant levels of impurities are introduced into the final ceramic structure because all the materials used in gel forming are organic in nature. Many ceramic materials in different compositions can be produced by using this method. It can also be adapted to many new materials and applications. Gelcasting has a wide application area. It can be used to produce materials 1 to 6 kg in weight with complex shapes involving thin sections down to about 0.2 mm. [1]. Up to now gelcasting method is applied to many ceramic powder systems such as alumina, aluminum nitride [7], boron carbide [8], ferrites [9], SiC [10], silicon nitride [11]. It is appropriate for producing large parts in a simple shape such as toroidal rings as well as small parts in complex shapes such as silicon nitride turbine rotors as shown in the two pictures on the left of Figure 1 [1].



Figure 1. Ceramic parts with complex shapes produced by gelcasting method [1].

Ceramic bodies having similar properties with the slip-cast or dry pressed bodies can be produced by gelcasting method. Gelcasting is the best method in several categories when it is compared to other ceramic forming methods such as slip casting, injection molding and pressure casting. This method facilitates the production of large ceramic components without defects or with low levels of defects that have good green and dry strength. It is very similar to conventional methods since the dispersants, processing aids and equipment are common in all these formation techniques [1].

Gelcasting process may be divided into two types according to the nature of the forming gel as traditional and thermoreversible gelcasting [2], the former being the original and the most widely applied one. Ceramic powder is mixed with a monomer solution to form a suspension. Polymerization starts by the addition of a chemical initiator and a catalyst to the slurry. Polymer gel network forms in situ and it makes it possible for the slurry to obtain the shape of the mold easily. Ceramic particles are immobilized due to the formation of a chemically cross linked gel. The gelcast green body is then removed from the mold followed by drying, thermal removal of the organic matrix and finally sintered. Drying must proceed slowly in order to prevent warping and cracking because of the high water content of the slurry. Thermal organic matrix removal proceeds relatively more rapidly due to the low organic gel contents [1-6].

Most commonly used monomers in traditional gelcasting are acrylamides such as methylacrylamide (MAM), methylene bisacrylamide(MBAM) and hydroxymethyl acrylamide (HMAM). Their initiator and catalyst are ammonium persulfate(APS) and tetramethylethylenediamine (TEMED). The presence of oxygen prematurely terminates free radical polymerization by reacting to form peroxide group at the end of the chain [1-6].

In this thesis study, the use of gelatin and carragenan gum as gel formers in the gelcasting of alumina was investigated. The effects of the gel former type and content during the gelcasting of green bodies on the mechanical behavior of alumina ceramics were investigated. Research on the use of these environmental friendly biopolymers appears to be promising and they are better choices for complex shaped ceramic item gelcasting applications. Other purposes of the study are those:

- To compare the performance of gelcasting method with other ceramic forming methods.

- To search for ways to reach high solid loadings in preparation of powder suspension.

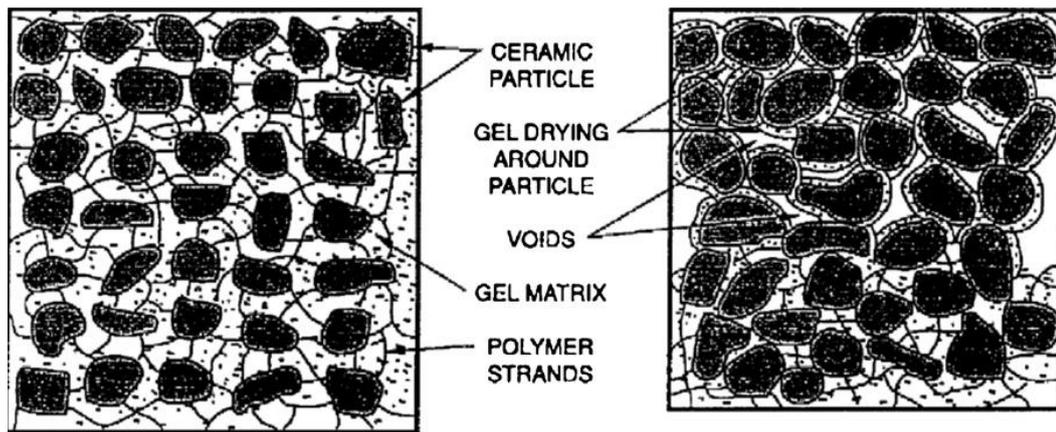
1. 1. Traditional Gelcasting Method

Gelcasting method is based on the principles of ceramic processing science and polymer chemistry. The use of a monomer solution in the preparation of the slip containing the ceramic powder and the appropriate dispersants generates the necessary flowability. Methylacrylamide (MAM) and methylbisacrylamide (MBAM) are generally the preferred monomer and crosslinker couple for traditional gelcasting. The most commonly used free radical initiator and catalyst are ammonium persulfate (APS) and TEMED [1-6].

Gelcasting process depends on the formation of a crosslinked polymer-solvent gel system. The prepared flowable slips can be readily poured into molds to form complex shaped parts. Monomer solution in the slip is polymerized and cross linked to form a gel. The polymerized gel matrix immobilizes ceramic particles and solidifies in the shape of the mold. Gelcast green body contains 15-20 wt% crosslinked polymer, dispersants and solvent. Gel used in gel casting is completely organic. This process can be used for casting any ceramic powder since the organic gel is non-ionic and doesn't adsorb to particle surface. The polymer fills the spaces and traps solvent molecules among its branches as a result of polymerization. Eventually, a high molecular weight polymer forms. Macroscopic result is a polymer-solvent gel [1-5].

Solvent is removed from gelcast green body by a drying stage. After drying process, cross linked polymer is removed from the part by binder burn-out process. Only 2-4 wt% of polymer with respect to ceramic powder weight is present in dried gelcast green body. This polymer content is similar to that of dry pressed green bodies. As a result of binder burn-out process, pore channels in the green body shift to the green body surface which may cause the formation of cracks [1-5].

After removal from mold, the gelled part contains about one-fourth of its mass as moisture, and the moisture is then removed by drying. A schematic microscopic view of the cross-section of wet and dried gelcast green bodies is shown in Figure 2 [4].



a Wet gelcast

b Dried gelcast

Figure 2. Magnified schematic representation of a microscopic cross-section of wet and dried gelcast parts [4].

As seen in Figure 2, particles get closer to each other while gel adsorbed around the particles loses its water. The evolution of the gel network during drying creates one of the significant benefits of gelcasting method in improving particle consolidation in the green structure [4].

The most critical step of gelcasting process is the preparation of a high solids loading slip of well dispersed particles. Slips can be prepared in an entirely closed system preventing the incorporation of impurities into the ceramic body. Furthermore high homogeneity should be achieved to produce good ceramic bodies. The flow chart of gelcasting method is given in Figure 3 [1-5].

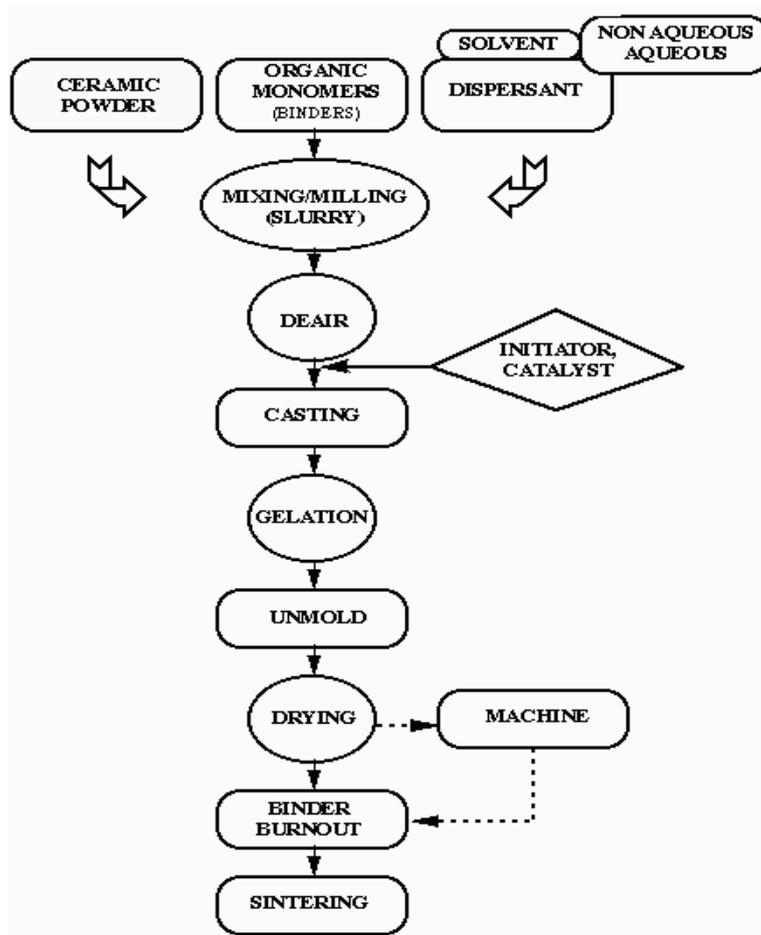


Figure 3. Traditional gelcasting flow chart [1]

1. 1. Slip Preparation

Important parameters in slip preparation for traditional gelcasting are: 1) Batch size 2) Ratio of powders 3) Densities of powders 4) Gel composition 5) Dispersant amount and density 6) Solids loading level of the slurry [1].

Commonly accepted slip preparation procedures in literature can be outlined to include the following steps. All liquid content (gel premix, dispersant and plasticizer) and half of the powder are charged into a ball mill with a volume of 4 liters. Batch is mixed in the ball mill for 2 hours at about 50-100 rpm. After the addition of another one fourth of the starting powder to the batch, the mix is ball milled at a high speed for another 2 hours. Finally, remaining $\frac{1}{4}$ of the powder is added to the batch and it is milled at a low speed of about 1-10 rpm. Addition of ceramic powder to the batch stage by stage is necessary to provide high solids loading. The rate of ceramic powder addition to the batch and the mixing time between additions varies with the nature of the

ceramic powder. For example, there are specific alumina powders which can be added to the mill in a single step [1].

The slip is transferred to an appropriate container after the milling/mixing operation and de-aired under vacuum by a mechanical pump. The removal of gas bubbles is facilitated by the addition of defoamers to the slip during deairing. De-airing is necessary in gelcasting process in order to produce high quality pore-free ceramics. After de-airing process is completed, a catalyst is added by vigorous mixing. 10 wt% of dispersant solution is added and the slip is de-aired again. Gel-cast slip is then cast into an appropriate mould. Cast ceramic ages at 50°C for 30-60 minutes. Gelation occurs at room temperature by the mechanism as given in Figure 4 [1].

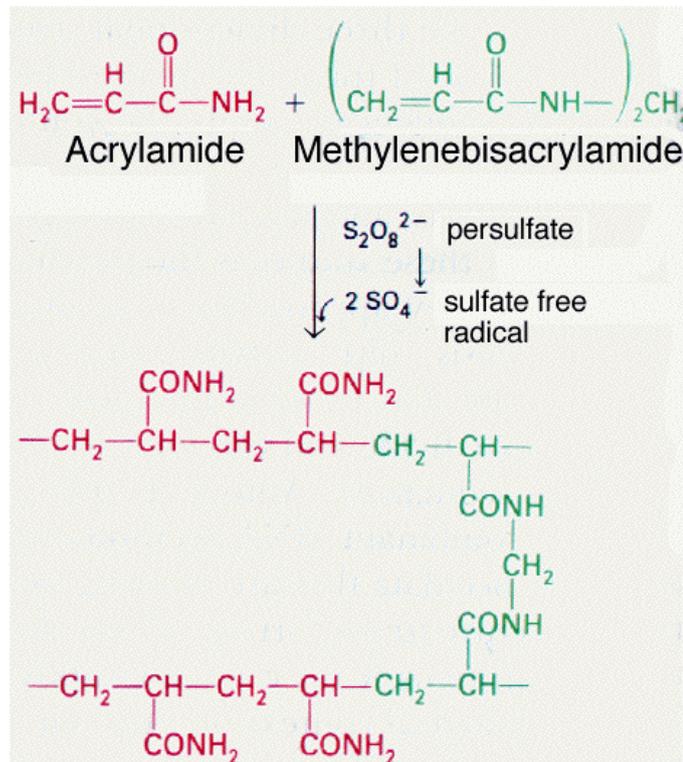


Figure 4. Gelation mechanism in traditional gelcasting [5].

The gelcast body can be easily removed from the mold after the mold is cooled. The cast green body is dried by traditional methods. Humidity controlled drying is necessary for large and thick ceramic articles.

1. 2. Importance of Solids Loading

In gelcasting process, slip density is the same with the density of green product like in injection molding and extrusion processes. It is therefore very significant to keep the solids content of the slip at a maximum level. This necessitates the preparation of flowable slips (viscosity 200-300 cp) that have solids content as high as possible. High solids loading lets us obtain green products that exhibit the lowest shrinkage during drying and these products have high density after firing. Moreover, low shrinkage on products during drying and firing decreases the problems resulting in warpage and cracking [1, 3, 5, 14].

The determination of a suitable dispersant and a mixing method is an initial prerequisite for the successful preparation of a high solids loading gelcasting slip. Most monomers are compatible with dispersants used in ceramic slip preparation. Therefore standard dispersants used in slip casting and spray drying can be used in gelcasting. Nevertheless, there are some differences between gelcasting and conventional slip-casting slip formulations. The most important difference between the two methods is that the solids loading needed for gelcasting is higher than that needed in slip-casting [1, 3, 5, 14].

Slurries should have 25-45 %vol. and 40-55 %vol. of solids loading for spray drying and slip casting respectively depending on the used powder and casting conditions. Solid loading of gel casting slurries is desired to be at least 50 vol%. In most conditions 50 %vol. of solid loading is obtained. Even 60 vol% of solids loading was also obtained and reported, but in some conditions sufficient solids loading cannot be obtained. For example, it is almost impossible to obtain a solids loading above 45 vol% in Ube E10 silicon nitride, stark B10 silicon carbide and TOSOH TZ zirconia powders. Dispersing these powders in water for any application is very difficult above the mentioned solids loading level. The reason for this mainly is due to the high particle surface areas of these powders [1].

For most ceramic powders, monomer system has no effect on dispersion because gelcasting monomers are non-ionic and don't adsorb on particle surfaces. The monomer system rarely plays a role in the dispersion of some powders. One of these powders is TOSOH TZ8YS zirconia powder. This powder can't be dispersed above 35 vol% in a monomer solution prepared with 15 wt% of MAM-MBAM or MAM-PEGDMA. But, in

a 20 wt% HMAM-MBAM monomer solution and without using dispersant, zirconia powder can be dispersed at 45 vol% solids content because the monomer solution behaves like a dispersant for the TZ8YS powder [1].

Gelcasting slips can be prepared by using different mixing equipment. Usually in slip mixing, low amount of mixing media is used relative to powder amount. For gelcasting slips, ratio of media and powder should be 0.5:1 or 1:1. This ratio provides the sufficient forces to well disperse the powder in water and braking soft agglomerates but it isn't enough for making particle size smaller. If it is desired to decrease particle size, media/powder ratios should be 10:1 or 20:1. [1, 14]

Achieving high solids loading also requires addition of ceramic powder to gelcasting batch incrementally. Half of the ceramic powder is added by to the batch including monomers, dispersant and water initially. The remaining powder is then added stage by stage as mixing continues. For powders that are hardly dispersed in water, additions can follow this path: $\frac{1}{2}$, $\frac{1}{4}$, $\frac{1}{4}$ or $\frac{1}{2}$, $\frac{1}{4}$, $\frac{1}{8}$, $\frac{1}{8}$ [6]. In order to obtain homogenous slip, powder particles should be wet completely and dispersed well [1, 14].

The last one or two additions to the mixture should be carried out at a low speed. Mixing can be again conducted at a high speed when addition of the powder is finished. Slow mixing allows the slip to flow. Mixing a dilatant slip fast makes the slip to stick on mill walls. In this condition, mixing doesn't occur. If the powder particles disperse in the slip well, viscosity starts to decrease with mixing and dilatancy disappears. After this point, mixing can be done at a high speed. [1,14]

1. 3. Traditional Gelcasting Molds

Mold selection, its production and use are important factors for successful gelcasting applications. Most commonly used mold materials for gelcasting are aluminum, glass, PVC, polystyrene, and polyethylene. Aluminum can easily be machined and is cheaper than other mold materials. Anodized aluminum as a mold material has good surface properties. The removal of gelcast article from the anodized aluminum mold therefore would be significantly easier. Plain aluminum may not be suitable for some gelcasting applications because gelcast items tend to stick to the mold surfaces [1-6].

Glass molds are commonly used to cast thin films and tubes. Gelcast pieces have a tendency towards easy removal from glass surfaces mainly due to the presence of smooth glass surfaces. Unfortunately, it is hard to machine glass which may not be useful for large scale production. PVC molds are usually used for producing bars, tubes and rings. PVC causes the formation of a thin ungelled layer on the surface of gelcast part. This ungelled layer makes the removal of the part from mold significantly easier by performing as a lubricant. The formation of an ungelled layer does not occur on the gelcast component surface when neoprene is used as a mold material. PE and PS molds are usually used to make test samples. PE and PS can also cause the formation of an ungelled layer on the gelcast article surface [1-3].

There are also special mold materials besides the above including meltable core materials, graphite, plaster and several other polymeric materials. Gelcast articles containing cores/holes can be obtained by using meltable cores such as wax inside the mold which melts at about 40-50°C. Melting temperature of the core material must be lower than that of gel casting solvent. Sometimes highly pure graphite molds are used to obtain pure ceramic parts. Graphite can readily be machined and molds with desirable properties can be prepared. Graphite molds necessitate the use of some oils to release the gelcast piece from the mold. These oils are usually silicone oils and organophosphate esters. In order to obtain a high purity in the ceramic part, 100% organic oils should be used in the molds [1-3].

Plaster molds are often used in slip casting of ceramics. The pores on the plaster mold surface unfortunately create problems in gelcasting. The presence of these pores and the capillary forces removes the water quickly from the gelcasting slurry which makes their use unsuitable for gelcasting applications. Polymeric molds are useful for gelcasting and the most popular casting molds are made of silicone rubber and urethane an example of which is shown in Figure 5. They cause the formation of ungelled 1-2 mm. thick layers on the surface of the gelcasting piece. Dissolved oxygen in silicon rubber prevents the gelation reaction. Silicon rubber molds should be gas free and gelcasting should be conducted in a nitrogen atmosphere [1-3].

Gelcasting slip can interact with the mold in several manners. An interaction occurs between the mold and the slurry as the casting slip wets the mold surface. Gelation of the slip causes the gelcast piece to adhere onto the mold surface. Interaction between the mold and the slurry can be adjusted by coating. These coatings are called as mold release agents. These are the substances such as waxes, oils, greases, polymer

dispersions, polymer resin solutions, fatty acids and inorganic powders. Many commercial mold releasing agents used in polymer processing are suitable for gelcasting. Mold releasing agent selection depends also on the geometry of the casting part as well as type of slip and the mold surface [1-3].

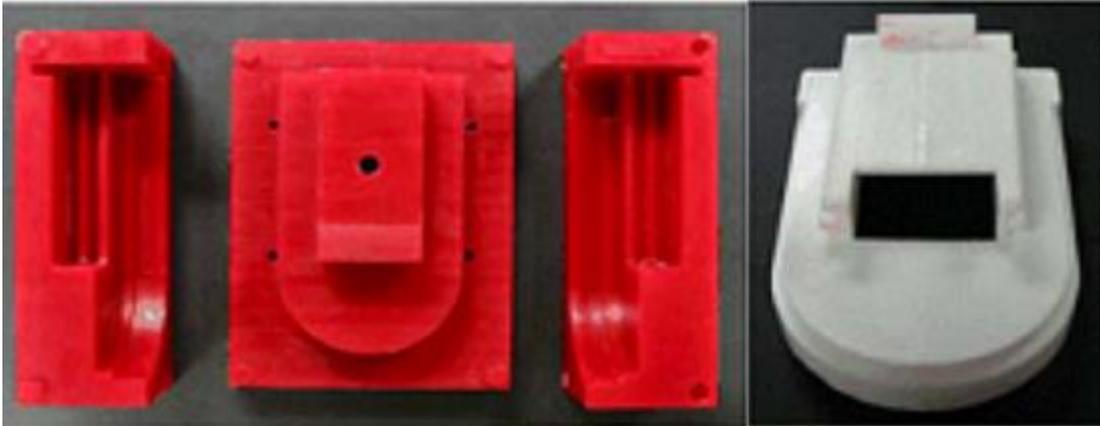


Figure 5. Polymeric gelcasting mold and the corresponding gelcast product [6].

1. 4. Binder Burn-out Process for Traditional Gelcasting

The polymeric gel network that exists in gelcast green body should be removed prior to sintering. The advantage of gelcasting method is the presence of relatively lower level of polymeric materials in the green body before thermal binder removal. Dried gelcast body contains 2-6 wt% of polymer relative to powder amount. A gelcast ceramic article contains only 5.5 wt% of organics [1-3] while an injection molded piece contains 27 wt% of polymer.

The decomposition temperature of a monomer gel in green gelcasting is mainly determined with thermal analysis. The thermal analysis results on ceramic gelcasting parts prepared with MAM-MBAM and MAM-PEGDMA gel systems generally indicated that decomposition of the gel is realized in the 250-650°C range. Silicon nitride powder accelerates decomposition of the gel. Plain monomer gel decomposes at 650°C, whereas monomer gel in silicon nitride gelcast articles decomposes at 550°C. [1-3]

Binder burn-out process in gelcasting is the same with the process in die pressing and iso-pressing. Polymeric content decompose at similar temperatures in the green bodies prepared by all three techniques. In certain applications where the gelcast

article is large and its thermal conductivity is low, a slow heating rate should be applied [1-3].

1. 5. Important Points at Traditional Gelcasting Process

Gelcasting is the production process of ceramic materials from submicron sized technical ceramic to mm sized refractory material powders. This process is convenient for producing ceramic parts in a wide range of sizes which may have complex shapes and thin walls. The green body becomes hard and stronger after gelation occurs in the gel-cast sample. The gel also brings particles closer to each other causing the formation of a closely packed green structure. High strength of green ceramic parts makes their machining possible [1-6].

Five important points should be taken into consideration to conduct a successful gelcasting application: The first of these is the necessity to prepare a highly dense gelcasting slip. Powder particles should be well dispersed and packed in the green body. Therefore, dispersing method and dispersing media used in slip preparation is very important. Second important point is about the choice of a suitable monomer and cross-linker combination. Monomer and cross-linker chemistry and their ratios determine the mechanical properties of the green body. Third point is about a suitable initiator and initiator concentration selection. This provides significant clues on the casting time determination. Another important point is the selection of a suitable mold material and mold releasing agent combination. This provides us to remove green body from the mold easily. The last consideration is the green gelcast article drying conditions which would cause a minimum level of stress formation, warpage and cracking [1-5].

1. 2. Thermoreversible and Natural Gelcasting Systems

Unlike the chemical cross linking occurring in traditional gelcasting, ABA-type triblock copolymers in a midblock-selective solvent form physical gels in which aggregated end blocks are linked by the well-solvated midblocks in thermoreversible gelcasting. While there are several examples of thermo-reversible triblock copolymer gels, the requirements of ceramic processing preclude many systems. The most successful systems for thermo-reversible gelcasting are acrylic systems with

poly(methyl methacrylate) (PMMA) end blocks and either a poly(n-butyl acrylate) (PnBA) or a poly(tert-butyl acrylate) (PtBA) midblock in ethanol, pentanol or 2-ethylhexanol (2EH) [2]. The gel formation in these systems is driven by the strong temperature dependence of the interaction between end blocks and solvent as seen in Figure 6 [2].

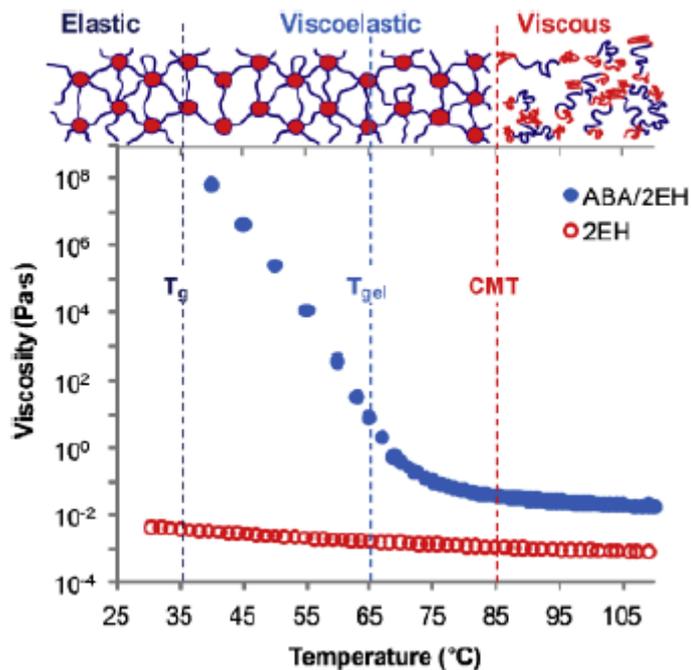


Figure 6. Viscosity of 2-ethylhexanol (2EH) and thermoreversible gel with 17.5 wt% A₂₅B₁₁₆A₂₅ in 2EH as a function of temperature. [2]

Also natural gels or binders used in gelcasting are placed in the group of thermoreversible (TRG) systems. These kinds of systems commonly consist of polysaccharides and other natural binders, gums etc. Several types of these such as starch, ovalbumin, chitosan, alginates, gelatin, carrageenan gum and etc. can be used in a natural gelcasting system. These systems are water soluble and therefore free of the environmental concern posed by alcohol solvents. Hydrated polysaccharides gel upon cooling by the formation of ordered, double helices, which revert to disordered, coiled chains upon reheating as shown schematically in Figure 7. Polysaccharides are complex carbohydrates formed from monosaccharides. Polysaccharides exhibit a large hysteresis between their gelling and melting temperatures. For example, the melting temperature of carrageenan gels is 20-25°C higher than the gelation temperature [2, 12-13].

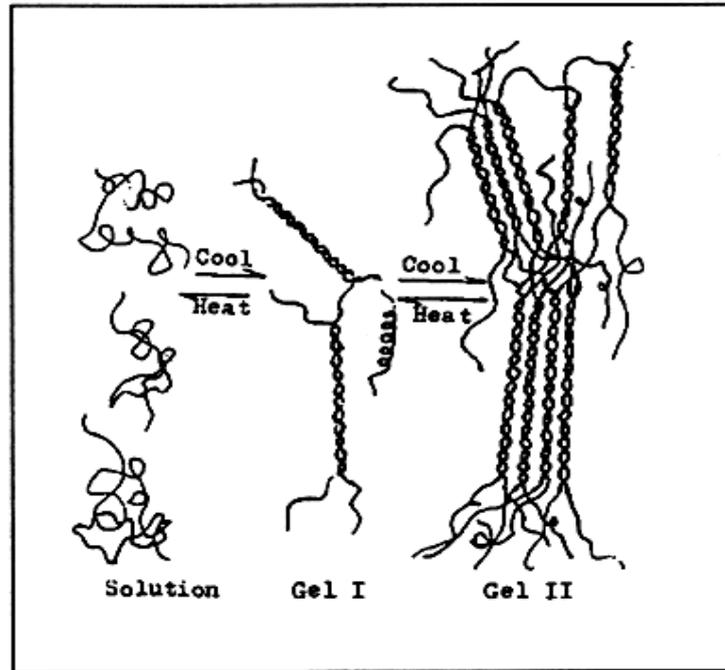


Figure 7. Gelation mechanism of polysaccharides [6]

Because TRG doesn't rely on polymerization, it can proceed in air. Gel reversibility allows for an infinite processing window and recyclability of flawed castings. Furthermore, monomers in general are very reactive. Many of the acrylate monomers used in traditional gelcasting is neurotoxic. The replacement of these with generally nonreactive and nontoxic long-chain polymers and polysaccharides increases safety. The disadvantage of TRG systems is the preparation of gelcast articles with lower green strength compared to those obtained through traditional gelcasting [2].

Some of the recent applications of natural biopolymeric systems in gelcasting of ceramic powders are summarized below.

Agarose (a polysaccharide) is a powerful gel former and its use in a solution causes viscosity to increase up high values. This also limits the content of agarose which can be used in gelcasting precursor solution. According to the study of I. Santacruz et al., in order to overcome this problem, pressurized conditions in a closed container where agarose more than its limited amount will be able to dissolve should be provided. The solubility of agarose in water is 3-4 wt% at about 100°C under atmospheric pressure but at 110-115°C, 5.6 wt% of agarose can be dissolved. This also increases the alumina solids loading in the gelcasting slip [21].

Alumina powder suspension becomes agglomerated upon excess amount of agarose addition and these agglomerates can not be removed by heating. This

agglomeration problem is not observed when agarose is added into powder suspension at 60°C in solution form [21].

Suspensions that have 80, 83 and 84 wt% α -alumina powder and varying amount of agarose between 3.5-5 wt% are prepared in the study of I. Santacruz et al. The prepared agarose solutions are added into the powder suspensions at the temperatures of 60-65°C. After gelcast green ceramic samples are obtained from powder/agarose mixture suspensions, these samples are sintered at 1500 °C for two hours. As a result, alumina ceramics are obtained with about 99% of densification [21].

The feasibility of the fabrication of complex shaped materials for high performance applications by using zirconia and agarose gel system is investigated in the study of Erik Adolfsson et al. Suspensions with 50 vol.% zirconia powder and 3 wt.% dispersant relative to water content are prepared. Solutions with 2 wt% agarose are prepared at 90-95°C. Powder suspensions and agarose solutions are mixed at 60-65°C [22]. According to the results of the study, gelcasting slurries finally have about 30 vol% of solids loading and 0.75 wt% agarose . The gelcast pieces maintain their shapes during densification and have near 99% of theoretical density. Product performance is close to the performance of the material produced by cold isostatic pressing [22].

A new gelcasting system is investigated in the study of Murat Bengisu, Elvan Yilmaz et al. Forming of gel is based on the reaction of a 1wt% chitosan solution in dilute acetic acid with glutaraldehyde. The purpose of this study is to optimize process parameters in a new chitosan based gelcasting system with ceramic oxide powders by using α -alumina and zirconia powders. Low molecular weight chitosan flake is used to prepare the chitosan solutions in acetic acid. Gelation of the chitosan solution is accomplished by using a 25 wt% aqueous glutaraldehyde solution [23].

Ceramic powders are added to the acetic acid solution followed by chitosan solution in the study of Murat Bengisu and Elvan Yilmaz et al. The stabilized slurry is de-aired under vacuum for 2 minutes prior to glutaraldehyde addition. The gelcast mix is poured into moulds after the addition of a predetermined amount of glutaraldehyde. The gelcast pieces in moulds are further dried in air for 3-4 hours. The optimum gel is formed by crosslinking of 1 ml. chitosan solution (1 wt%) in 1 vol% acetic acid with 2 vol% glutaraldehyde (25 wt%).

Glutaraldehyde is a very toxic and corrosive substance. A low pH value is desired for stabilization of the ceramic slurry. However, low pH value increases the gelation time. Gelation is obtained at ambient temperature in these systems [23].

As a result of this study, a simple gelcasting process is developed for alumina and zirconia using chitosan-acetic acid solutions containing 48-50 vol% ceramic powders and crosslinking at ambient temperature. According to the study, dense crack free ceramics with smooth surface are produced from alumina powders but the production of similar ceramics from zirconia powder can't be possible. This is attributed to the better flow properties of the alumina slips [23].

In the study of Santanu Dhara and Parag Bhargava et al., ovalbumin(egg white) is used as gel former in gelcasting of alumina powder. Liquid ovalbumin-water premixes are prepared in different ratios and mixed with alumina suspensions. Then some measurements are made to understand the relative influence of ceramic solid loading and ovalbumin content on slurry rheology [24]. Subsequently prepared slurries are tape-casted on thin PET sheets. Obtained green alumina tapes have a uniform microstructure and are quite flexible. The minimum thickness achieved in the sintered tapes is around 60 μm and densification percentage of sintered tapes is about 95% [24].

There are also some research about using of sodium alginate and calcium iodate in gelcasting of ceramics. Alginate is a type of gelling polysaccharide which can be dissolved in water at room temperature. It is gelled by cross linking with divalent metal ions at increased temperature. Divalent cations, especially calcium ion facilitate to form particularly strong chelation complexes by combining regions of polysaccharide.

In the study of Z. Yu et al., the gelling properties of sodium alginate solution and resulting suspension with ceramic powder are investigated. Near net shaped green bodies are produced by gel casting process. Firstly sodium alginate solutions in different concentrations are prepared by stirring in de-ionized water at room temperature. As a result of rheological measurements it's found that viscosity of the solution with 3 wt% alginate has a maximum value at the shear rate of 35s^{-1} [25]. In order to examine the controlled gelling process of calcium and alginate, 1 wt% of calcium iodate is dispersed in the 3 wt% alginate solution by stirring. By rheological measurements, calcium iodate amount in the mixture is determined. After process parameters are determined, ceramic samples are produced by forming process using the controlled reaction between alginate and calcium iodate.

In conclusion calcium iodate is successfully used for the forming process of green body from ceramic suspension containing sodium alginate. The solubility of the divalent salt can be controlled by heating rate and final temperature. Gelling process by reaction of alginate with calcium ion is completed fast and wet green body is formed at

a shorter time, typically in the range of about 30 min to 2 h from casting to demolding. In addition, polymer sodium alginate is less expensive, which makes it possible to use in large scale production [25].

In this thesis study, gelatin and carragenan gum were selected as gel formers. Their effects on mechanical behavior of alumina ceramics were investigated. Properties of these two natural gel formers will be given below.

2. 1. Gelatin

Gelatin is obtained by a controlled hydrolysis of the fibrous insoluble protein, collagen, which is widely found in nature and is the major constituent of skin, bones and connective tissue. Being a protein, gelatin is composed of a unique sequence of amino acids [15]. Characteristic features of gelatin are the high content of the amino acids such as glycine, proline and hydroxyproline. Structurally, gelatin molecules contain repeating sequences of glycine-X-Y triplets, where X and Y are frequently proline and hydroxyproline [16]. These sequences are responsible for the triple helical structure of gelatin and its ability to form gels where helical regions form in the gelatin protein chains immobilizing water.

2. 2. Composition and Some Properties of Gelatin

Gelatin contains a large number of glycine, proline and 4-hydroxyproline residues. A typical structure is: Ala-Gly-Pro-Arg-Gly-Glu-4Hyp-Gly-Pro- as seen in Figure 8 [15]. Gelatin melts to a liquid when heated and solidifies when cooled again. It forms a semi-solid colloid gel when coupled with water. Gelatin forms a high viscosity solution in water which sets to a gel on cooling, and its chemical composition is closely similar to that of its parent collagen. Gelatin is also soluble in most polar solvents [15-16].

Gelatin gels exist over only a small temperature range, the upper limit being the melting point of the gel, which depends on gelatin grade and concentration (but is typically less than 35°C) and the lower limit the freezing point at which ice crystallizes.

Mechanical properties of gelatin gels are very sensitive to temperature variations, previous thermal history of the gel and time. The viscosity of the gelatin/water mixture increases with concentration and when kept cool ($\approx 4\text{ }^{\circ}\text{C}$) [15-16].

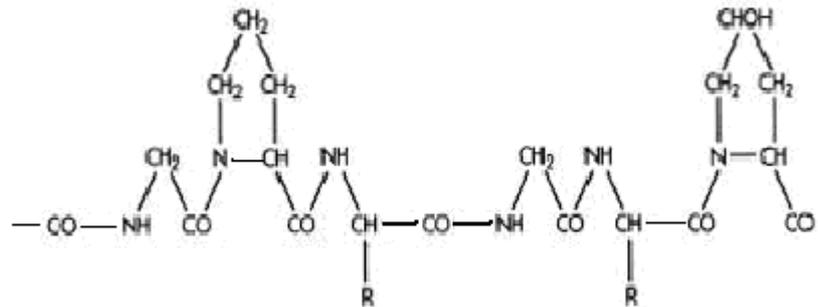


Figure 8: Chemical structure of gelatin [15]

2. 3. Some Technical Uses of Gelatin

Its best known utilization is as gelling agent in cooking. Different types and grades of gelatin are used in a wide range of food products. Also it is used for the clarification of juices, such as apple juice and vinegar. Certain professional and theatrical lighting equipment use color gels to change the beam color. Furthermore, gelatin is closely related to bone glue and is used as a binder in match heads and sandpaper [15-16].

2. 4. Carrageenan Gum

Carrageenan gum is a kind of natural gum obtained from seaweeds. Natural gums are polysaccharides of natural origin, capable of causing a large viscosity increase in solution, even at small concentrations. In the industry they are usually used as thickening agents, gelling agents, emulsifying agents, adhesives, binding agents, flocculating agents, foam stabilizers, etc [17].

Carrageenans or carrageenins are a family of linear sulfated polysaccharides that are extracted from red seaweeds. Gelatinous extracts of this seaweed have been used as food additives for hundreds of years. Carrageenan is a vegetarian and vegan alternative

to gelatin. Carrageenans are large, highly flexible molecules that curl forming helical structures. This gives them the ability to form a variety of different gels at room temperature. They are widely used in the food and other industries as thickening and stabilizing agents. A particular advantage is that they are pseudoplastic and they thin under shear stress and recover their viscosity once the stress is removed [17-18].

All carrageenans are high-molecular-weight polysaccharides made up of repeating galactose units and 3,6 anhydrogalactose (3,6-AG), both sulfated and nonsulfated (Figure 9). The units are joined by alternating alpha 1–3 and beta 1–4 glycosidic linkages.

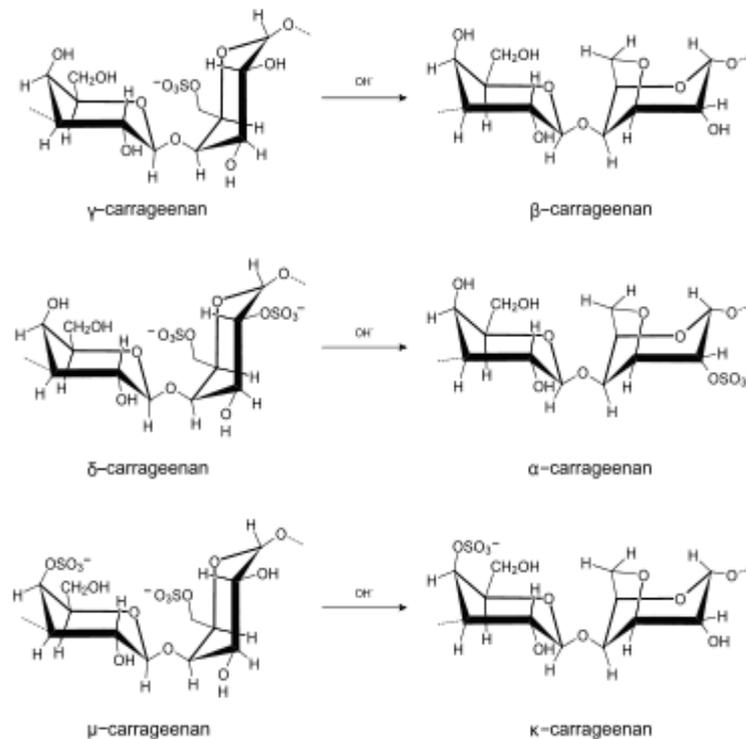


Figure 9. Different types of carrageenans[18]

1. 3. Some Applications of Alumina Ceramics

Al_2O_3 is widely used as an abrasive due to its hardness and strength. It is less expensive substitute for industrial diamond. Many types of sandpaper use aluminium oxide crystals. Its low heat retention and low specific heat are the reasons behind its wide use in grinding operations particularly cutoff tools. Because of its high wear resistance, it can be used in so many different areas such as scratch repair kit in CD/DVD, tooth polisher in toothpaste, coating material in aluminum and grinding media in ceramic ball-mill.

Aluminium oxide is an electrical insulator used as a substrate for integrated circuits but also as quantum tunneling barrier films for the fabrication of superconducting devices such as single electron transistors and superconducting quantum interference (SQUID) devices. In addition it is also used to make spark plug insulators [19-20]. Mechanical properties of the alumina used in this study are given in the Table 1 below.

Table 1. Mechanical properties of 99.5% alumina [30]

| 99.5% Aluminum Oxide | | | |
|----------------------|----------------------------------|-----------|------------|
| Mechanical | Units of Measure | SI/Metric | (Imperial) |
| Density | g/cm^3 (lb/ft^3) | 3.98 | (242.8) |
| Porosity | % (%) | 0 | 0 |
| Color | — | ivory | — |
| Flexural Strength | MPa ($lb/in^2 \times 10^3$) | 379 | 55 |
| Elastic Modulus | GPa ($lb/in^2 \times 10^6$) | 375 | (54.4) |
| Shear Modulus | GPa ($lb/in^2 \times 10^6$) | 152 | 22 |
| Bulk Modulus | GPa ($lb/in^2 \times 10^6$) | 228 | 33 |
| Poisson's Ratio | — | 0.22 | (0.22) |

(cont. on next page)

Table 1 (cont.)

| | | | |
|---------------------------------------|---|------|------|
| Compressive Strength | MPa (lb/in ² x10 ³) | 2600 | 377 |
| Hardness | Kg/mm ² | 1440 | — |
| Fracture Toughness K _{IC} | MPa•m ^{1/2} | 4 | — |
| Maximum Use Temperature | °C (°F) | 1750 | 3180 |

CHAPTER 2

EXPERIMENTAL PROCEDURE

2. 1. Materials

There are mainly three types of materials used in the experiments. These are alumina powder, gelatin and carrageenan gum. Main purpose of this study was to determine the effects of gelatin and the gum on mechanical properties of the gelcast alumina ceramics. All materials are commercially available. Alumina powder is Alcoa 1550 in high purity. Gelatin is a commercial food grade powder gelatin obtained from Merck. Carrageenan gum is also commercial and its name is Carrabind MPF 60B. Gelcasting slips were prepared by using de-ionized water and a commercial dispersant. Powders were well dispersed by using a commercial Dolapix CE64 dispersant which is an aqueous solution of the ammonium salt of polymethacrylic acid (PMAA-NH₄).

2. 2. Method

The experimental study can be outlined into three main parts. These are the experimental design, gelcasting of alumina ceramics by using two different gel formers and the mechanical testing of the green and sintered ceramics.

2. 2. 1. Rheometric Analysis of Gelatin

Gelatin-water solutions with gelatin contents in the 3-7 wt% range were prepared. Then they were rheologically analyzed in order to see how gelatin amount and temperature affect viscosity of the solution. Analysis was conducted with rheometer equipment Haake Mars with temperature controlling system.

2. 2. 2. Experimental Design

Experimental design includes determination of factors, their levels and responses on which the factors affected and finally type of the design. Furthermore, determining factors and other things requires a pre-experimental study. In the present experimental design there are two factors affecting responses. These are the solids loading of alumina powder and gelatin amount. There are four responses. These are material properties: bending strength, compressive strength, hardness and density as %TD (relative to the theoretical density of alumina 3.98 g/cc). The effects of the two factors on these ceramic material properties were investigated.

Small alumina-gelatin samples were prepared in different compositions with gelcasting method during the preliminary experimental work. It was observed that the casting slip lost its' flowability and became inconvenient for gelcasting above 53 vol% of solids loading. Thus, levels of solid loading factor below 53 vol% were chosen. Furthermore, it was observed that excess amount of gel former causes serious problems during the mixing of the solutions for the formation of the castable slip resulting in poor homogeneity. Also obtained slip was not useful for casting because of its high viscosity. Therefore, limit for gelatin amount was chosen as 6 wt% of water present in a batch. Previous research on ceramic gelcasting with gelatin gel former supports this finding [28, 29]. Carrageenan gum amounts were also chosen empirically. Previously, some gum-water solutions were prepared with an increasing gum amount. Maximum solubility of carrageenan gum in water was investigated. It was determined that carrageenan gum amount should be below 2 wt% of water present in a batch.

A general full factorial design was conducted in this work. Factorial design can be important in determining the relations and the interactions between factors which may not be apparent. Three levels of solids loading as 47, 50 and 53 vol% and four levels of gelatin gel former content as 0, 3, 4, 5 and 6 wt% were selected as the design parameter values. A total of 21 runs were planned without replication of the runs. This design including 4 responses would totally yield 84 pieces of data by the end of the experimental work. Experimental design is further summarized in Table 1. Similar alumina solids loading levels were used in the gelcasting experiments with carrageenan gum being the gel former. A total of 15 gelcasting runs were conducted at the selected gum levels of 0, 1, 1.4, 1.7 and 2 wt%. Characterizations towards the determination of

similar responses with the previous gelatin gelcasting experiments were conducted. This experimental design is further tabulated in Table 2 which indicates a total of 60 characterizations.

This work differs from previous research since it involves an extensive investigation of the mechanical properties of the gelcast alumina ceramics prepared by different levels of gelatin or gum gel former in the gelcasting process.

Table 2. Design of experiment table for the experiment

| Factors | Levels | Responses | Factors | Levels | Responses | |
|--------------------|--------|----------------------|----------------------------|-------------|----------------------|----------|
| Solid loading vol% | 47 | Bending strength | Solid loading vol% | 47 | Bending strength | |
| | 50 | | | 50 | | |
| | 53 | Compressive strength | | 53 | Compressive strength | |
| Gelatin amount wt% | 0 | | Carrageenan gum amount wt% | 0 | | |
| | 3 | | | 1 | | |
| | 4 | | Hardness | 1.4 | | Hardness |
| | 5 | | | 1.7 | | |
| | 6 | Density %TD | 2 | Density %TD | | |

2. 2. 3. Sample Preparation and Mechanical Tests

Two different approaches were used in the preparation of gelcasting slips. The alumina powder suspension and the gelatin or carrageenan gum solution were prepared separately and the uniform gel former solution was added to the hot alumina suspension at 60°C in the first method. Alumina powder suspension had about 55-56 vol% of solids loading amount. This amount was kept constant for each gelcasting slip prepared. Then water amount of the gel former solution was changed with respect to the desired solids loading amounts and gel former weight percentages. Gel former solution with maximum 24-25 wt% of gel former amount was prepared for gelatin whereas it was prepared with maximum 2.5-3 wt% of gel former amount for carrageenan gum at about 90-100 °C. Weight percentage of gel former is determined with respect to the weight of total water in final mixture. Amounts of the materials used in gelcasting slip preparation were given in Appendix A.

A hot gelatin solution with the necessary amount of water was prepared initially and the alumina powder was added to this uniform gel former solution in the second method. Water amount of the hot gel former solution was kept constant and alumina powder amount that will be added into gel former solution was adjusted with respect to desired solids loading amounts. Mixing was conducted in an ultrasonic bath in both methods. A certain amount of dispersant (Dolapix) was added in proportion to the alumina powder amount for obtaining a well dispersed suspension. Dolapix was used for the steric stabilization of the alumina powders in both methods used in gelcasting slip preparation. Processing flowsheet is schematically given below in Figure 10. The gelcasting slips were poured into plexiglass and pasteboard molds as seen in Figure 11.

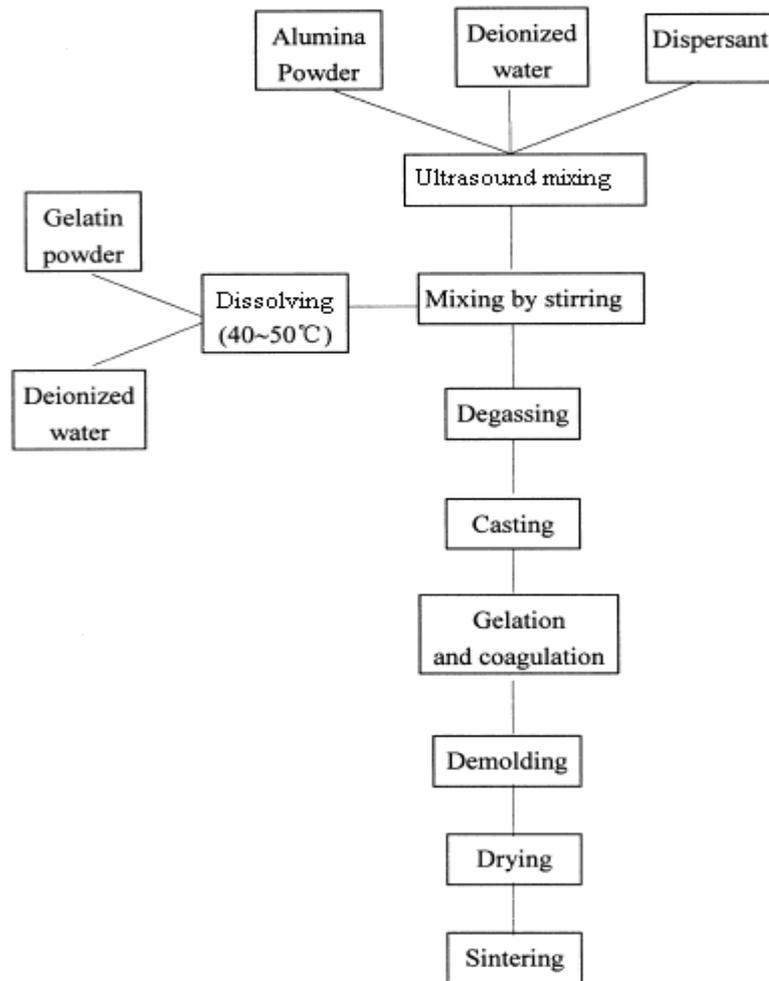


Figure 10. Experimental flow chart according the first method of gelcasting slip preparation

a)



b)



Figure 11. a) Plexiglass molds b) Pasteboard molds

They stay in mold until gelation occurs and then dry. The gelation and drying took about 4 days for large samples and 2 days for small samples. The large blocks were especially placed in a refrigerator (approximately 4°C) for 1-2 days in order to speed up the cooling of the cast part and the gelation process. After large green samples were taken out the molds, they were left for drying one day more. Then, half of small green samples were sintered at 1550°C. Molds were in different shapes due to the mechanical tests that will be applied on. The pictures of gelcasted green samples are seen below in Figure 12.

a)



b)



c)



d)



Figure 12. a) Coin like green alumina samples. b) Cylindrical green alumina samples. c) Green alumina large blocks. d) Green alumina bars after cutting from the green alumina blocks.

Coin-like small samples were prepared for density and hardness measurements. Two groups of coin like alumina green samples including gelatin and carrageenan gum were subjected to Vickers microhardness test. The test was carried out with the equipment Time microhardness tester. Totally five indents were formed in each composition of the samples applying a 9.8 N of load with a square based diamond pyramid indenter. Resulting indents were viewed with optical microscope and diagonal lengths of each were measured. Eventually, microhardness of each sample was determined.

Vickers hardness number (VHN) is defined as the load divided by the surface area of the indentation. It is computed using the following equation:

$$VHN = \frac{2P \sin(\theta/2)}{L^2} = 1.854P/L^2 \quad (2.1)$$

Where P is the applied load (kgf), L is the average length of the diagonal (mm) and θ is the angle between opposite faces of diamond (136°).

Cylindrical samples were prepared for compression test according to ASTM (C773-88) standards [19]. Cylindrical green and sintered alumina samples were subjected to compression test by the Universal Test machine. Each sample was compressed until their fracture occurred. The force versus stroke data was obtained for each sample. This data were transformed to stress-strain diagrams and maximum compressive strength values were determined.

Gelcast green bodies were prepared in rectangular prism like large blocks. These blocks were cut into small bars in 3 x 4x 50 mm dimensions for 3-point bending test according to ASTM (C1161-94) standards [26].

Sample preparation for 3-point bending test especially very tedious and took a lot of effort and time. Precision cutting of small bars from large alumina blocks was conducted with difficulties. A significant number of the blocks were broken and became useless during precision cutting into small test bars. A few or insufficient number of bars could be cut from some blocks. Meanwhile, most of the cutting discs were fractured because of their thin structure. They were really sensitive to pressure. Nevertheless, finally a sufficient number of 3-point bending test samples could be obtained. Some pictures of the test samples are seen in Figure 13 below.

a)



b)



c)



d)



Figure 13. a) Green alumina test samples b) Sintered alumina test samples c) Sintered alumina test samples d) Alumina test samples are being prepared for density measurements.

After the head of the Universal Test machine was changed with 3-point bending test apparatus, the tests were conducted. Green and sintered alumina bars were broken from their middle points and maximum force values applied by the machine were monitored. Bending strength values of each sample were calculated according to the following formula:

$$S = \frac{3PL}{2bd^2} \quad (2.2)$$

Where P is the break load (kgf), L is the outer (support) span (mm), b is the specimen width (mm) and d is the specimen thickness (mm).

Plaster molds were prepared for the alumina slips that contain no gelatin or gum. They were prepared in suitable shapes for casting coin like and cylindrical samples as seen in the Figure 14. After plaster molds were obtained, alumina slips without any gel were poured into them. After the slips were dry in the molds, they were removed from the molds by breaking the molds.

a)



b)



c)



d)



Figure 14. a, b) Making plaster molds. c, d) Plaster molds were dried and then alumina slip casted.

Subsequent to the drying of alumina samples prepared with and without gel, half of them were sintered at 1550°C. Other half was kept at room temperature for mechanical property characterization of the green bodies.

CHAPTER 3

RESULTS AND DISCUSSION

Characterization of the alumina powder was conducted in the initial phase of the work before gelcasting experiments. As a result of phase analysis of the powder by XRD, it was determined that the powders' XRD peaks exactly matched to the standard alumina peaks (Figure 15). There were no peaks which could be attributed to the impurity phases. Particle size distribution analysis was conducted with Zetasizer Dynamic light scattering analyzer. Particle size of the alumina powder had a distribution between 250 and 500 nm as seen in Figure 16. BET surface area of the powder was determined as 5.8m²/g. A total weight loss of about 0.5% by weight with temperature up to 800°C was observed as given in the TGA curve in Figure 17. Up to 400-450°C, decrease in powder weight occur due to removal of physical water in the powder.

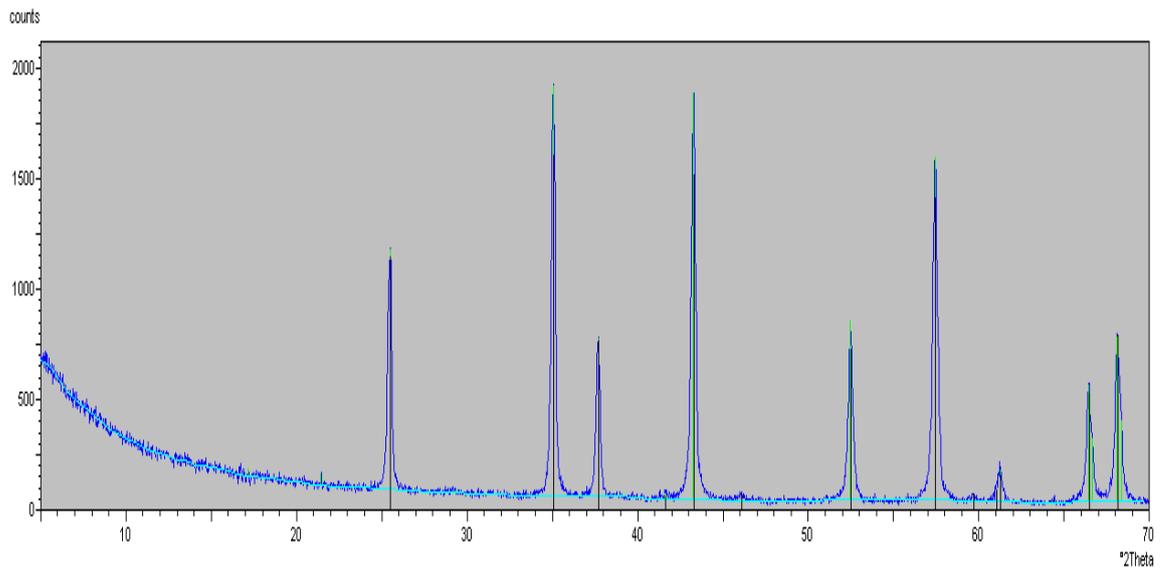


Figure 15. XRD analysis result of the alumina powder.

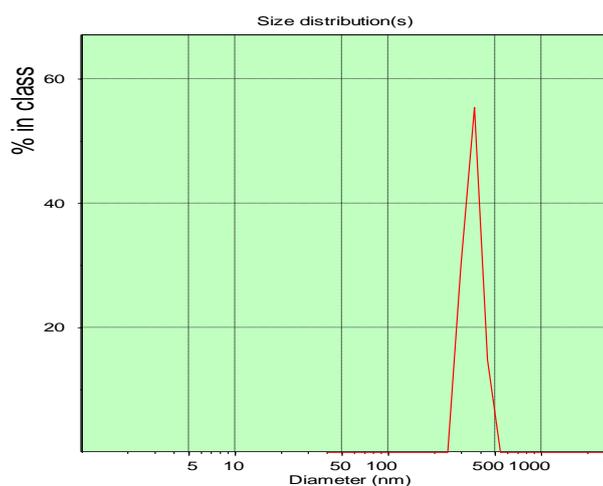


Figure 16. Particle size distribution of the alumina powder.

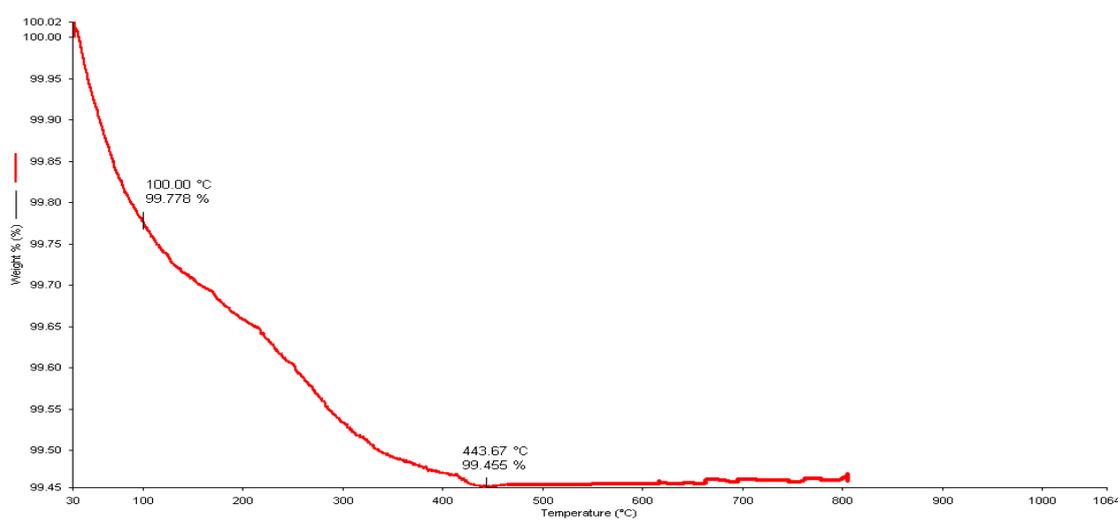


Figure 17. TGA analysis of the alumina powder.

Gelatin and carrageenan gum were both commercially available materials which can be easily dissolved in hot water. Their dissolution temperature in water is approximately 80°C. They form gels at about 30°C upon cooling.

3.1. Rheometric Analysis of Gelatin

Gelatin-water solutions with gelatin contents in the 3-7wt% range were prepared. Then they were respectively tested in the rheometer equipment Haake Mars. The viscosity change upon cooling from an initial temperature of 50°C was determined. The variation of the viscosity with gelation content upon cooling down to about 10°C is shown in Figure 18.

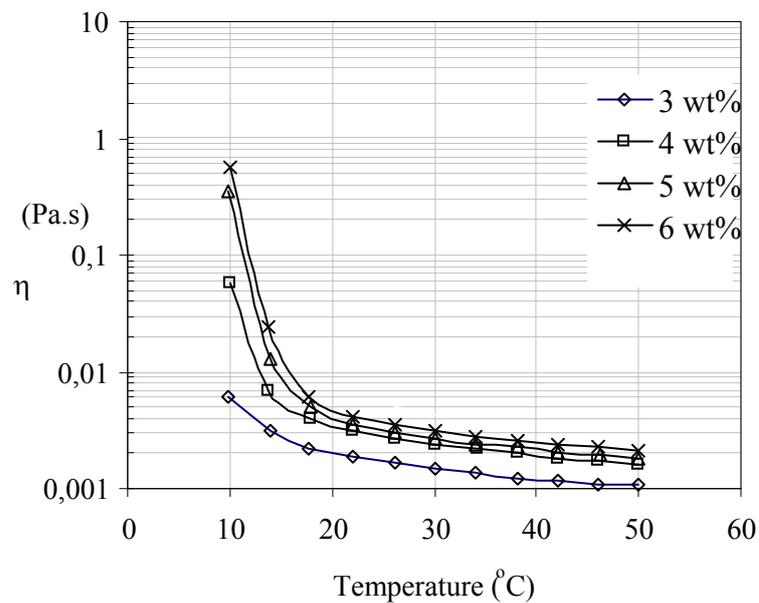


Figure 18. Change in viscosity of the gelatin solution with gelatin content upon cooling from 50°C to 10°C.

According to the graph, it can be said that actual gelation occurs below 20°C during cooling. A gradual increase can be seen in the viscosity of the suspensions up to 20°C, but they increase sharply below that temperature down to 10°C. It is obviously seen that by increasing the gelatin amount, gelation will be able to occur at higher temperature.

3.2. Density Measurements of the Samples

Small coin-like samples were prepared by gelcasting method as seen in Figure 19. They include gelatin in varying ratios from 3 to 6 wt% and also they have varying alumina solid loading amounts between 47 and 53 vol%. They were fired at about 1550°C. The sintered densities of the alumina ceramics were determined by using Archimedes method. The sintered densities of the samples are tabulated in Table 3.

Table 3: Sintered densities of the samples after sintering at 1550°C.

| Samples | | Av. Density %TD after 1550°C sintering |
|-----------------------------|----------------------|--|
| Solid loading amount (vol%) | Gelatin amount (wt%) | |
| 47 | 3 | 93.16 |
| 47 | 4 | 94.08 |
| 47 | 5 | 94.79 |
| 47 | 6 | 94.55 |
| 50 | 0 | 95.82 |
| 50 | 3 | 90.28 |
| 50 | 4 | 93.77 |
| 50 | 5 | 95.80 |
| 50 | 6 | 93.63 |
| 53 | 3 | 90.15 |
| 53 | 4 | 92.29 |
| 53 | 5 | 93.04 |
| 53 | 6 | 88.02 |



Figure 19. Sintered alumina samples.

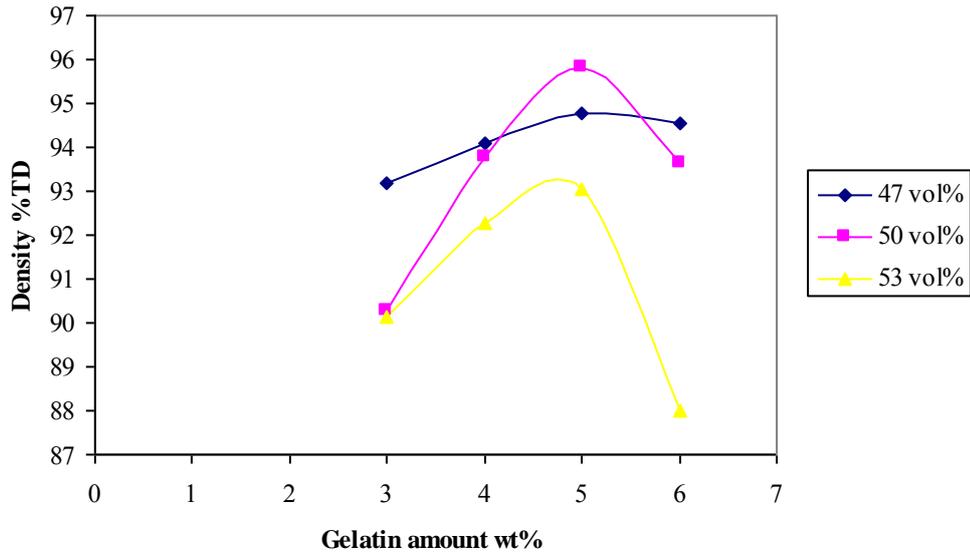


Figure 20. The variation of %TD with gelatin content and solids loading.

According to graph in Figure 20, generally as the gelatin amount of samples increases, an increase is also seen in their densification percentages. Nevertheless at all solids loadings, a sharp decrease was observed in the densities over 5wt% gelatin content. A maximum sintered density of about 95-96%TD was obtained at 5 wt% gelatin content. Porosity increased with increasing solids loading for most of the samples. At high levels of solids loading, it is harder to obtain a well dispersed of slip due to incomplete breakdown of the agglomerates of submicron alumina powder particles. This causes the introduction of large pores in the green body and those pores were not eliminated during sintering. Furthermore, during mixing more bubbles remained in the viscous slip as the solids loading increased. Density of the final product decreases with increasing level of closed porosity mainly due to the two problems stated above. The highest sintered density obtained for gelcast alumina samples were obtained with 50 vol% of solids loading and 5 wt% of gelatin content as 95.8%TD. In the study by L.J. Vandeperre et al., 98%TD sintered density for gelatin-gelcasted alumina ceramic with 45-50 %vol. of solid loading and 3wt% gelatin content was obtained. Sintering of the samples was conducted at 1575°C with 2 hour hold [28]. However, in the study by Yali Chen et al. maximum theoretical density was reported as 96.5% for gelcasting alumina ceramic with 50 vol% solids loading and 5 wt% gelatin content [29]. The sintered densities of the gelcast alumina ceramics prepared in this work were comparable with the reported values of previous research.

3.3. Hardness Measurements of the Samples

Hardness indents were viewed with optical microscope and diagonal lengths of each were measured. Then, microhardness numbers of each sample were calculated. The optical microscope images of some of them are seen in Figure 21 and resulting data on Table 4.

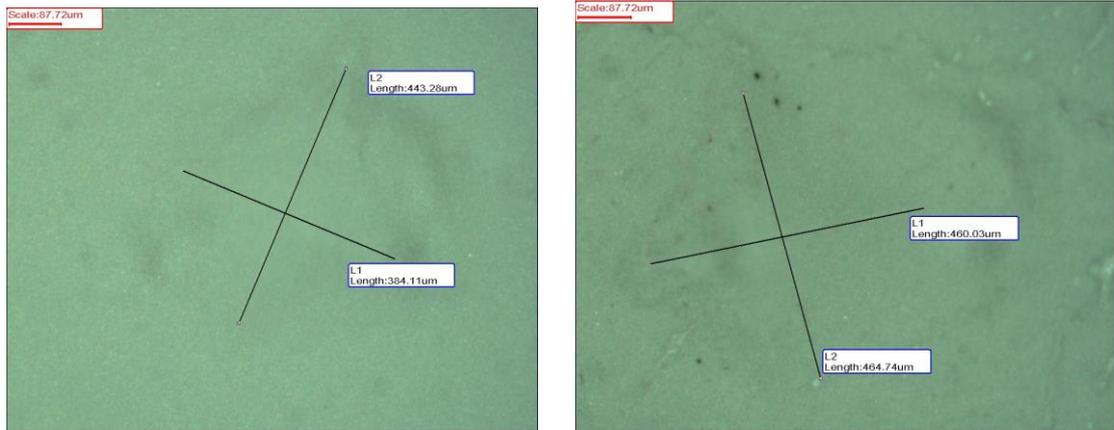


Figure 21. Optical microscopy images of the gelcasted green alumina samples. The indents of diamond pyramid indenter are seen.

Table 4: Vickers hardness numbers of green alumina samples gelcasted with gelatin and carrageenan gum.

| Sample | | Ave. Vickers Hardness Number | Sample | | Ave. Vickers Hardness Number |
|-----------------------------|----------------------|------------------------------|-----------------------------|------------------------------|------------------------------|
| Solid loading amount (vol%) | Gelatin amount (wt%) | | Solid loading amount (vol%) | Carrageenan gum amount (wt%) | |
| 47 | 3 | 105.83 | 47 | 1 | 79.27 |
| | 4 | 110.49 | | 1.4 | 35.28 |
| | 5 | 121.62 | | 1.7 | 52.37 |
| | 6 | 100.83 | | 2 | 66.87 |
| 50 | 3 | 99.06 | 50 | 1 | 81.23 |
| | 4 | 112.94 | | 1.4 | 69.91 |
| | 5 | 104.05 | | 1.7 | 72.55 |
| | 6 | 140.72 | | 2 | 49.77 |
| 53 | 3 | 93.99 | 53 | 1 | 42.49 |
| | 4 | 143.88 | | 1.4 | 48.7 |
| | 5 | 104.27 | | 1.7 | 40.89 |
| | 6 | 127.28 | | 2 | 51.23 |

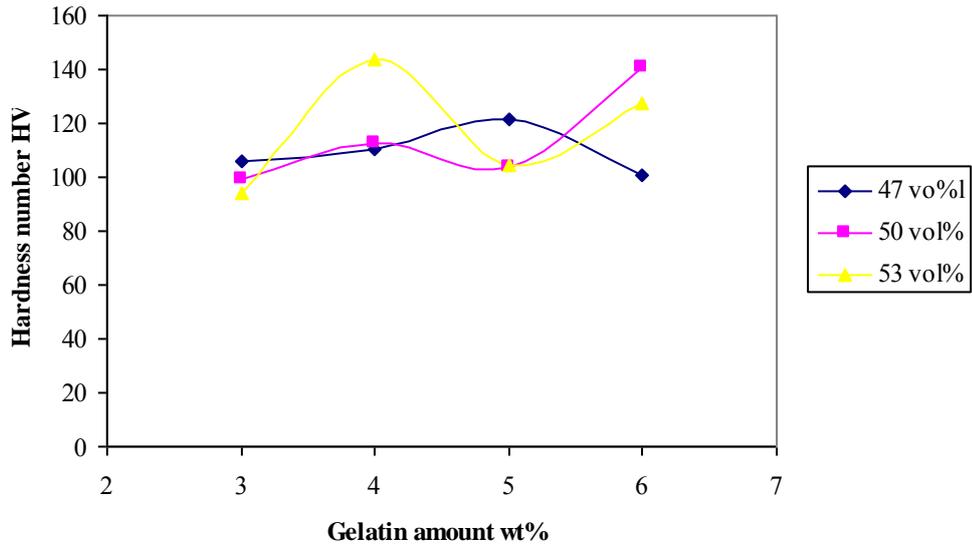


Figure 22. The graph of change in hardness of green samples due to their gelatin and alumina amounts

According to graph belonging to gelatin-gelcasted green alumina samples in Figure 22, hardness data were randomly distributed so a certain relationship isn't seen between hardness number and alumina amount. Also there is seen a very slight relationship between hardness number and gelatin amount. If the fluctuations are ignored, last hardness values of 50 and 53 vol% of solid loadings have increased with respect to their first values. Hardness number of the gelcasted alumina green samples changes between 80 HV and 145 HV. Maximum hardness number is 140.72 HV and it belongs to the sample with 50 vol% of alumina and 6 wt% of gelatin.

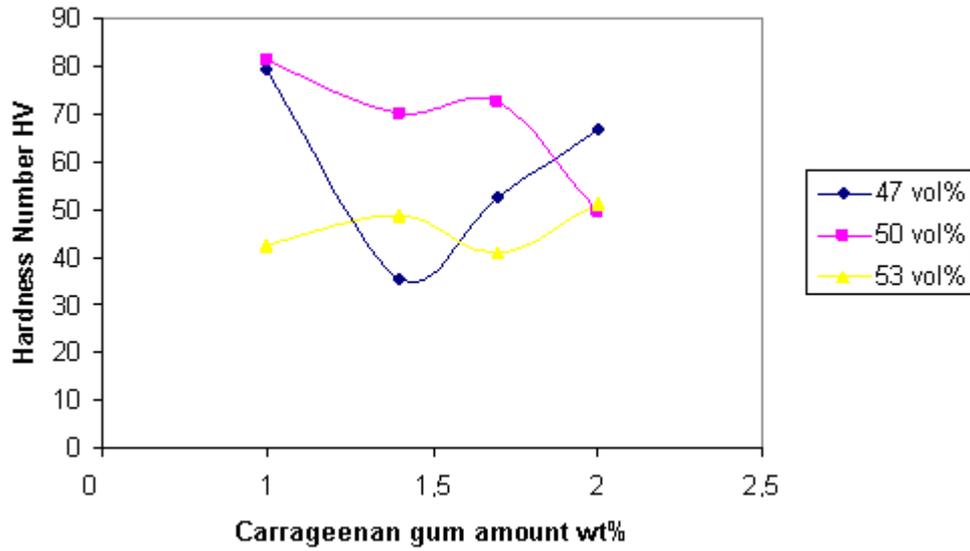


Figure 23. The graph of change in hardness of green samples due to their carrageenan gum and alumina amounts

According to graph belonging to gum-gelcasted green alumina samples in Figure 23, data are randomly distributed, we can't tell about a certain relation between carrageenan gum and hardness number. Maximum hardness number of the alumina green samples is 81.23 HV. Hardness number of the samples gelcasted with gelatin is higher than that of samples gelcasted with carrageenan gum. It means that gelatin is more effective on hardness of alumina ceramics.

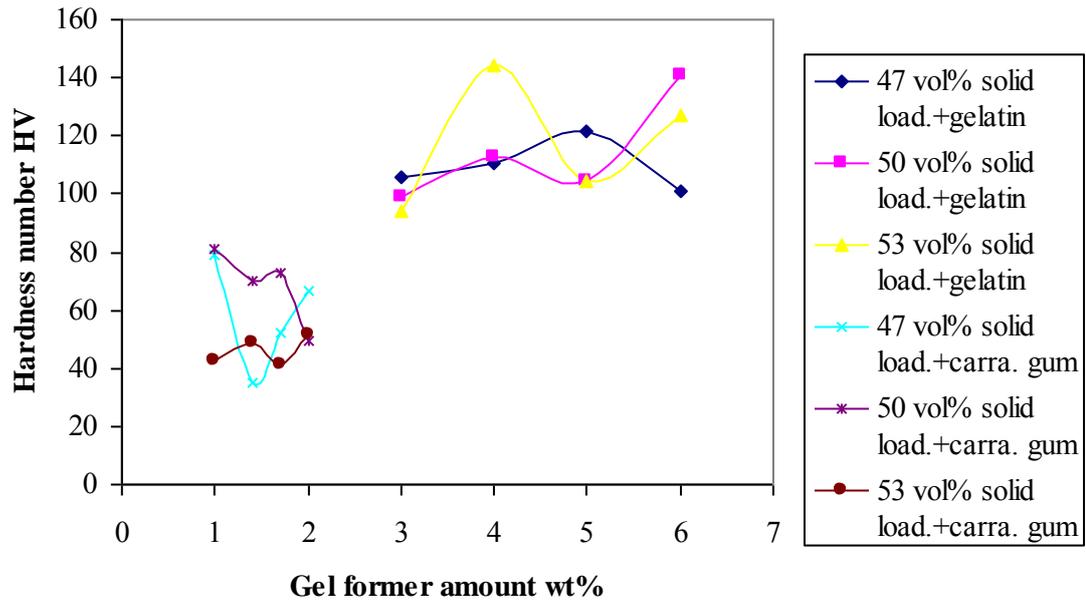


Figure 24. Comparison of gels used in alumina sample production regarding hardness

In the Figure 24, we can make the comparison of hardness values of alumina green samples gelcasted with gelatin and carrageenan gum that are added in a range of adjusted levels. It's easily seen that hardness numbers of green samples gelcasted with gelatin are greater than the samples gelcasted with carrageenan gum. As a result, gelatin is more effective on hardness of green alumina samples than carrageenan gum.

3. 4. Shrinkage Measurements of the Samples

Alumina ceramic slips were gelcasted with gelatin as large parts as seen in the Figure 25.a. Then green samples were cut into small bar pieces for 3-point bending test. Before cutting, their shrinkage amounts after sintering had to be taken into account. Because, dimensions of the samples should be in 3x4x50 mm according to ASTM 3-point bending test standard. Thus, previously small cubic pieces were cut from large green alumina parts as seen in the Figure 25.b. Then they were sintered at 1600 °C and shrinkages in their each dimension were measured and their shrinkage ratios calculated.

At the end of the calculations, shrinkage percentage after sintering was found as approximately 17.5%. Solid loading and gel amounts didn't have a significant effect on shrinkage, so their effects were neglected. This value was accepted as same for each composition. The study of Yali Chen et al. also supports this founding. In their study,

gelatin-gelcasted alumina samples have linear shrinkage of 15-16% during sintering [29]. During drying of gelcasted green ceramics, there weren't significant shrinkages in the dimensions of samples.

a)



b)



Figure 25. a) Green large alumina ceramics. b) Sintered small rectangular alumina pieces.

3.5. Compressive Strength Measurements of the Samples

After compressive testing of each sample, their force due to stroke data were obtained. These data were transformed to stress-strain diagrams and maximum compressive strength values were found. The change in compressive strength of green and sintered alumina samples due to their gelatin and alumina amounts are seen in the Figure 19-20.

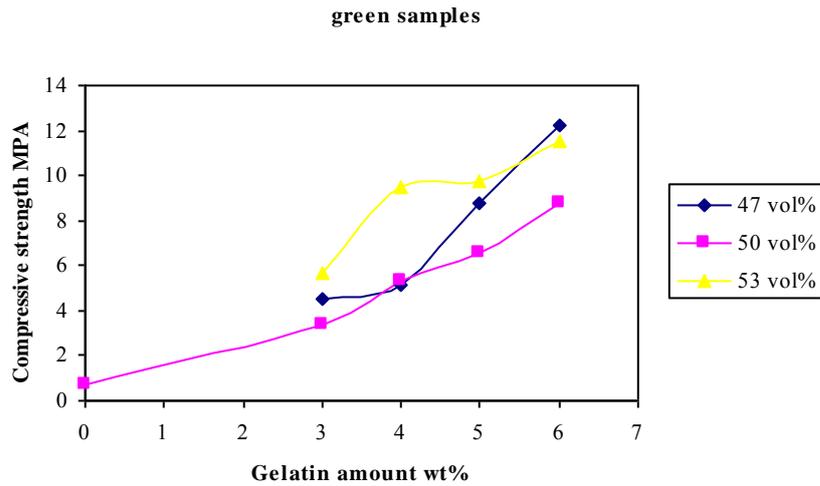


Figure 26. The graphs of change in compressive strength of green samples due to their gelatin and alumina amounts.

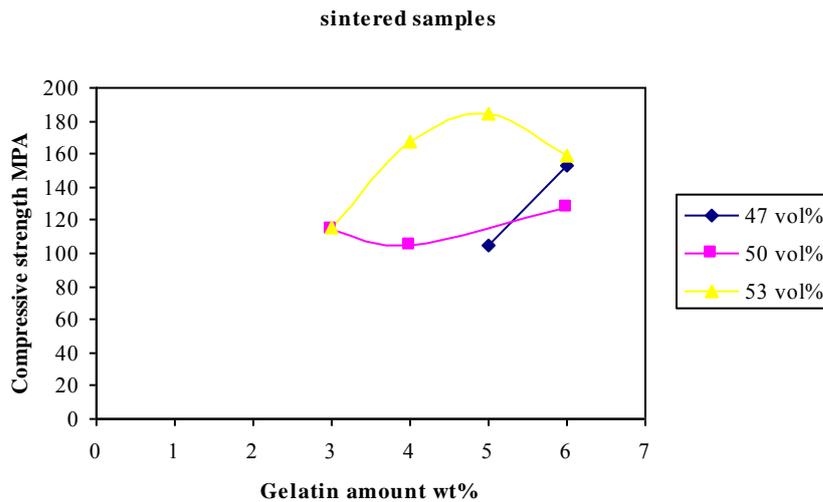


Figure 27. The graphs of change in compressive strength of sintered samples due to their gelatin and alumina amounts.

According to Figure 26, compressive strength of the green samples generally shows an increasing tendency due to increasing gelatin and alumina amounts. Measured compressive strength values of the green samples change between 2 and 12 MPa depending on varying compositions. In the study by L.J. Vandeperre et al. for 1 wt% of gelatin, green strength of the alumina samples is found between 3 and 5 MPa and it is said that these values are sufficient for green machining of the samples [28].

According to Figure 27, compressive strength of sintered samples shows a slight increasing tendency due to increasing gelatin amounts but only compressive strength of the samples with 53 vol.% of alumina solid loading shows a slight decrease after its gelatin amount goes up to 5 wt%. This finding supports the Y. Chen et al. finding. According to the study of Y. Chen et al. a suitable gelatin content for suspensions of 50±53 vol% alumina powder is determined as 4±5wt% (based on water) [29]. Excess amount of gel former causes decreasing in strength.

According to the graphs in Figure 26-27, maximum compressive strength of the green samples is about 12 MPa. After sintering of the samples, their compressive strength becomes 15 times greater and reaches to about 184 MPa.

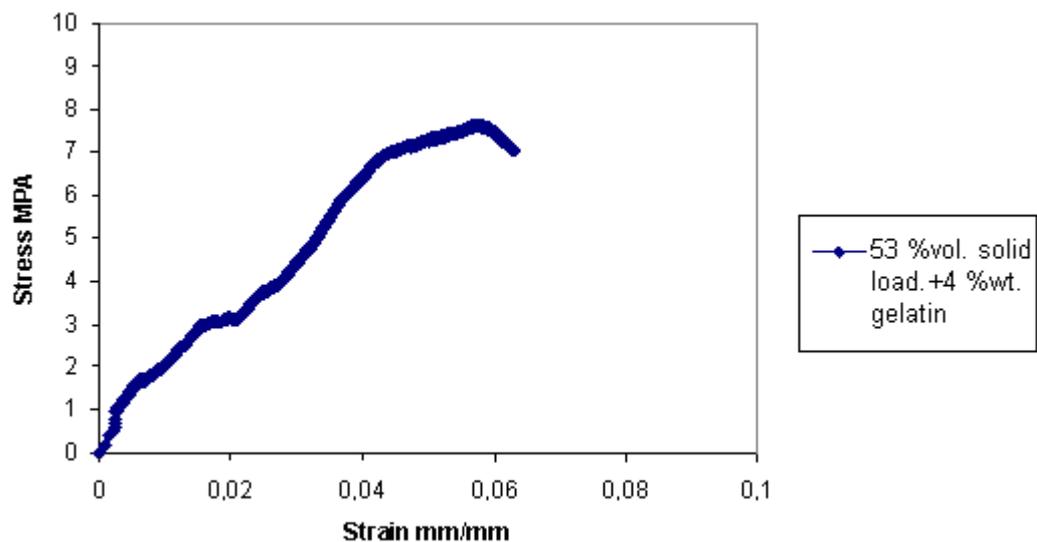


Figure 28. Stress-strain diagram of a green sample obtained as a result of compression test

You'll see the stress-strain diagram of a green sample including 4 %wt. of gelatin and 53 vol% of alumina content in the Figure 28 above. It shows maximum 7.5 MPa of compressive strength then, it is seen yielding and finally fracture of the sample due to excess strain.

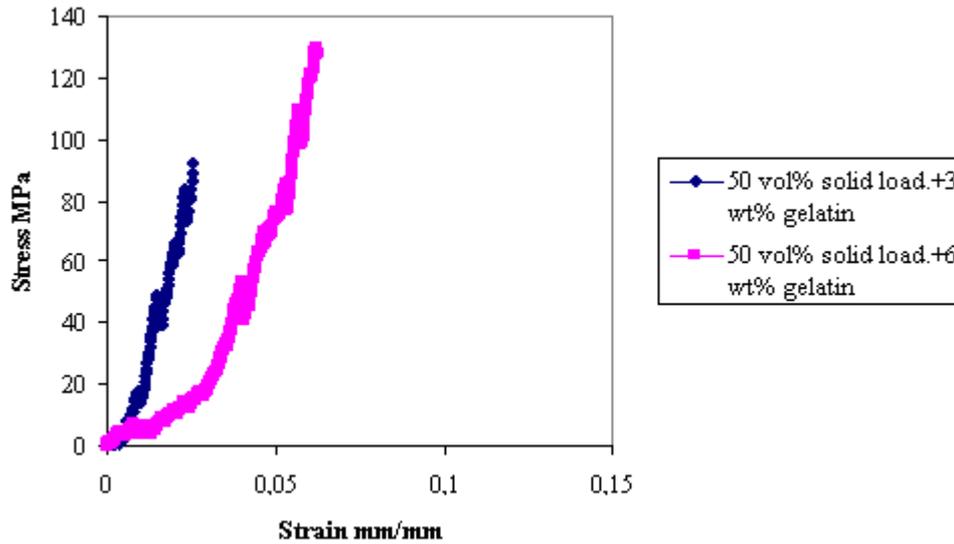


Figure 29. Stress-strain diagram of two sintered alumina samples obtained as a result of compression test

In the Figure 29, we see the stress-strain diagrams of two sintered samples. Their maximum compressive strength seems between 90 and 130 MPa. Furthermore, the effect of gelatin amount on compressive strength can be obviously seen. As the gelatin amount is doubled, compressive strength goes up from 90 to 130 MPa.

As compared with Figure 28, great effect of sintering is seen on compressive strength. Compressive strength of the samples has increased from about 7 MPa to 130 MPa after sintering. It means that their compressive strength became 18.5 times greater.

Alumina samples gelcasted with carrageenan gum were also subjected to compression test. Resulting data were collected and analyzed. Finally, some stress-strain diagrams were drawn and maximum strength values of the samples calculated. The compressive strength versus carrageenan gum amount graphs of the green and sintered alumina samples are seen in the Figure 23-24.

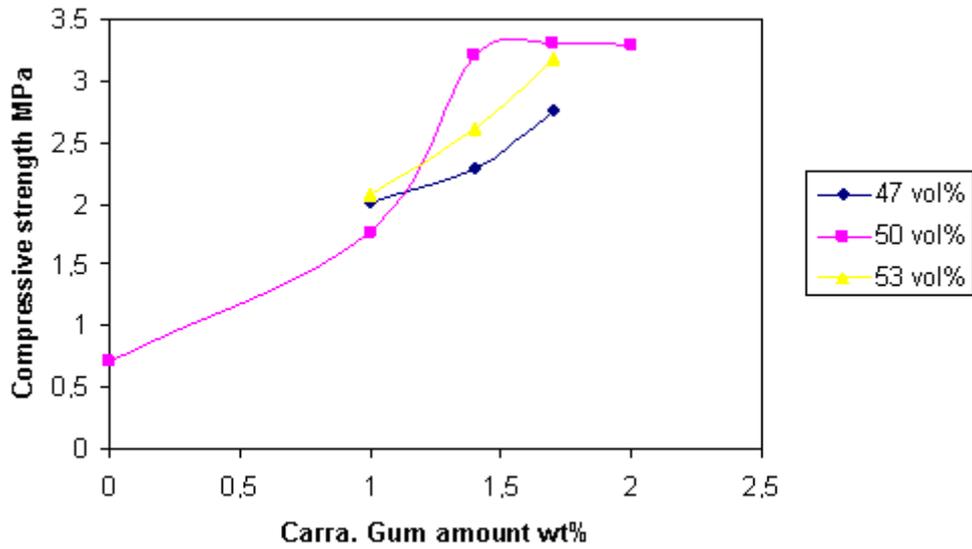


Figure 30. The graphs of change in compressive strength of green samples due to their carrageenan gum and alumina amounts.

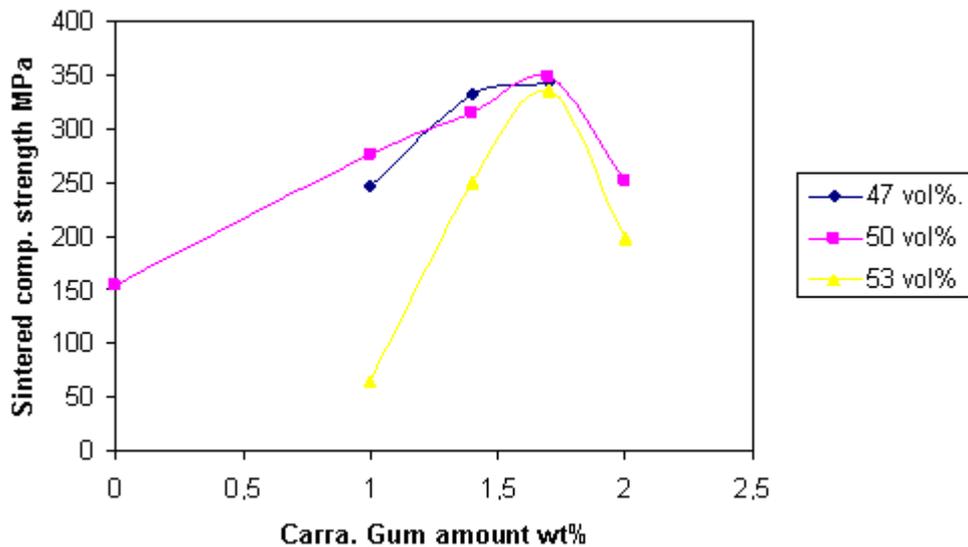


Figure 31. The graphs of change in compressive strength of sintered samples due to their carrageenan gum and alumina amounts.

According to the graph in the Figure 30, it's generally seen that when the amount of carrageenan gum present in green alumina samples increases, compressive strength increases too. Especially, gelcasted green alumina sample with 50 vol.% of solid loading reaches to 3.31 MPa which is the greatest compressive strength value

among the green alumina samples at 1.7 wt% of carrageenan gum amount. The strength increasing effect of alumina content on compressive strength could not be clearly observed. Before sintering, compressive strength of the gelcasted sample with 47 vol% of solid loading is below the those of others with higher solid loading, but after sintering its compressive strength increase above those of the other ones. The reason of this may be that particles in the slip with low solid loading are better dispersed and don't become agglomerate. Less bubbles form during mixing. Due to less bubbles, less porosity occurs in final product. By sintering, less porosity is more easily removed than the others containing more porosity.

The graph in the Figure 31 also supports the compressive strength increasing effect of carrageenan gum. Increase in compressive strength of sintered samples until 1.7 wt% of carrageenan gum amount is seen. After that point a decrease occurs in their compressive strengths. The point 1.7 wt% of gum amount seems like an optimum point in the graph. Again maximum compressive strength value belongs to the sample with 50 vol. of alumina solid loading and 1.7 wt% of carrageenan gum. It is 347.43 MPa. The effect of alumina content on compressive strength is also unclear according to the graph.

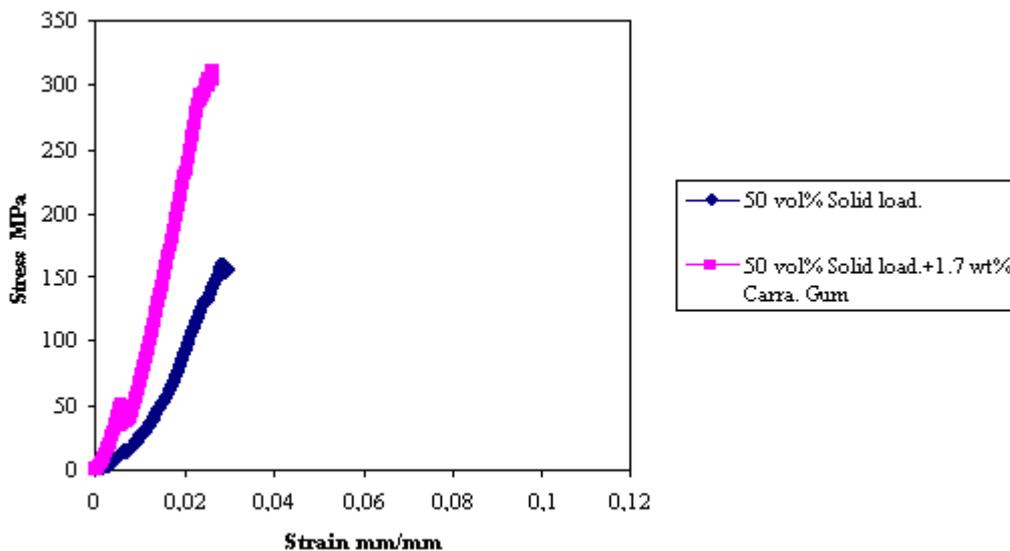


Figure 32. Stress-strain diagram of two sintered alumina samples obtained as a result of compression test

The stress-strain diagram of two sintered alumina samples obtained as a result of compression test is seen in Figure 32. One of the samples includes 1.7 wt% of carrageenan gum and other one doesn't include any. This graph shows us the effect of carrageenan gum on compressive strength more clearly. By adding 1.7 wt% of carrageenan gum to alumina ceramic body, its compressive strength raises up from about 150 MPa to 300 MPa.

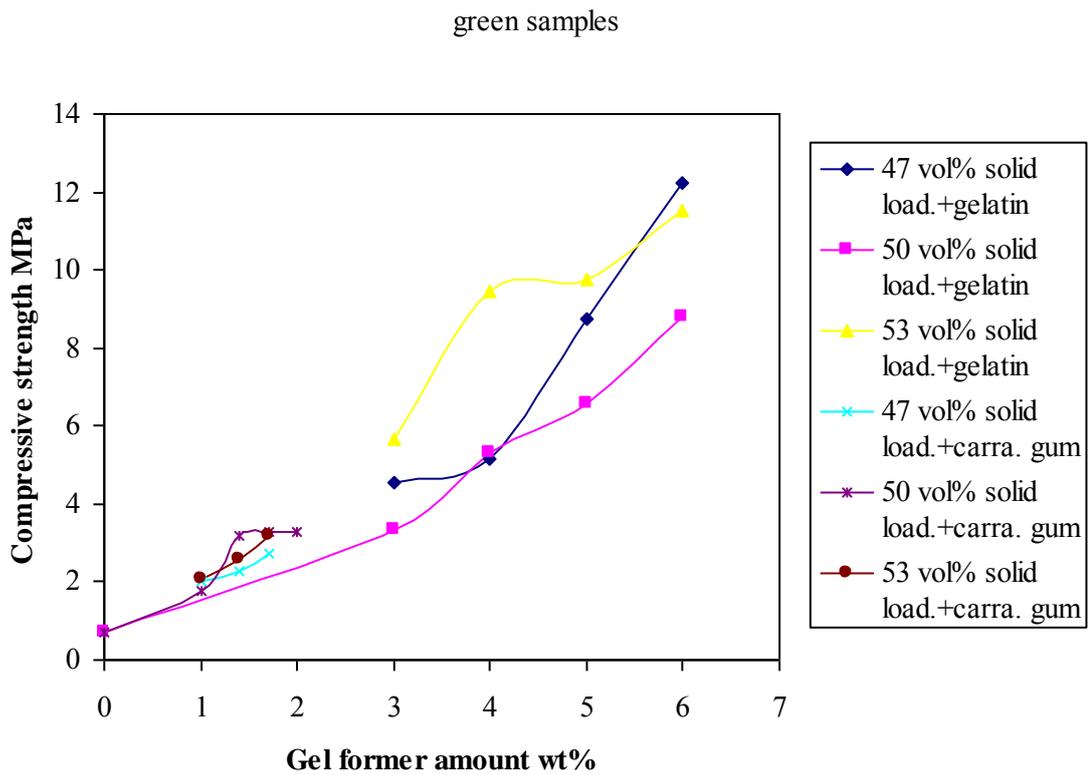


Figure 33. Comparison of gels' effects on green alumina samples regarding compressive strength

sintered samples

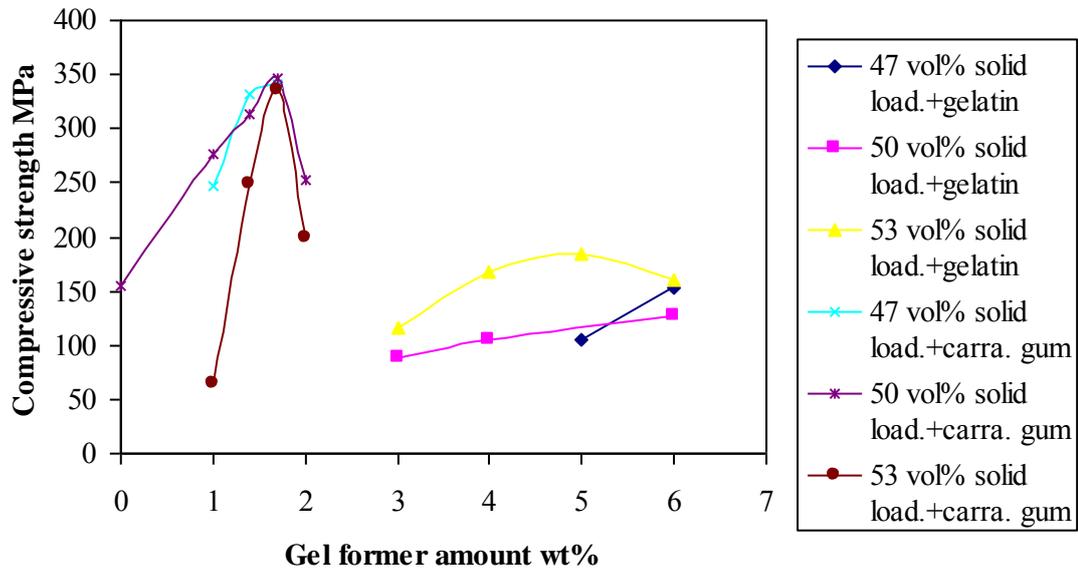


Figure 34. Comparison of gels' effects on sintered alumina samples regarding compressive strength

The comparison of the gels used in production as a compressive strength point of view is seen in Figure 33-34. Compressive strength of green alumina samples gelcasted with gelatin is greater than that of ones gelcasted with carrageenan gum (Figure 33). It's seen that after sintering of green alumina samples, compressive strength of the samples gelcasted with carrageenan gum becomes greater than ones gelcasted with gelatin (Figure 34). I think it can be interpreted such that: carrageenan gum formed more porosity in green alumina body than gelatin did. However, sizes of formed pores in the green alumina body may be much smaller in comparison to pores existing in gelatin gelcasted green body. Thus, the pores in gum-gelcasted green body could be removed easier by sintering in comparison to gelatin-gelcasted green body. As a result, sintered gum-gelcasted alumina samples had less porosity and thus it was stronger than the sintered gelatin-gelcasted alumina samples.

3.6. Three-point Bending Test of the Samples

Green and sintered alumina bars were broken from their middle points and maximum force values applied by the machine were monitored. After 3-point bending testing, maximum force values applied to each samples by the test machine were monitored. Resulting data were analyzed and results were obtained. Finally bending strength versus gelatin amount graphs for green and sintered samples were drawn in Figure 35-36.

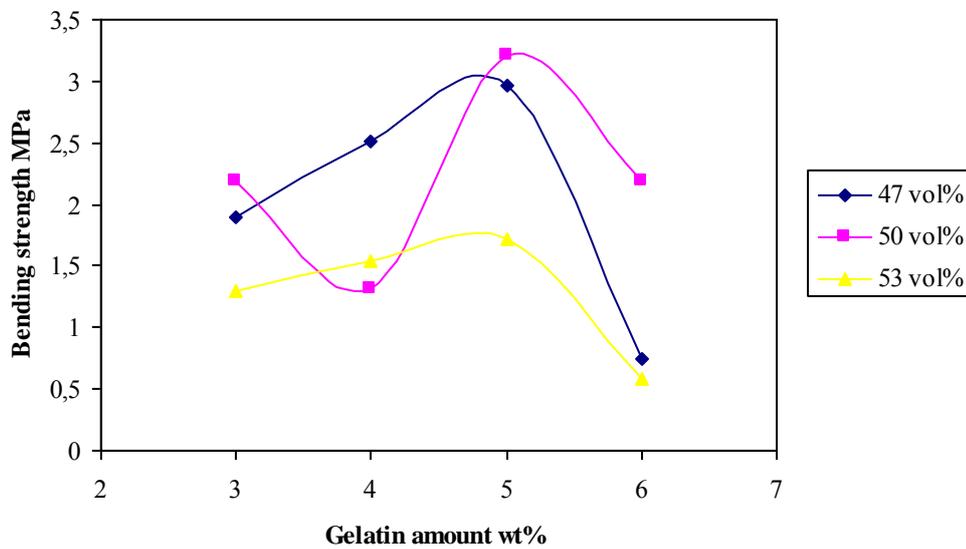


Figure 35. The graphs of change in bending strength of green alumina samples due to their gelatin amounts

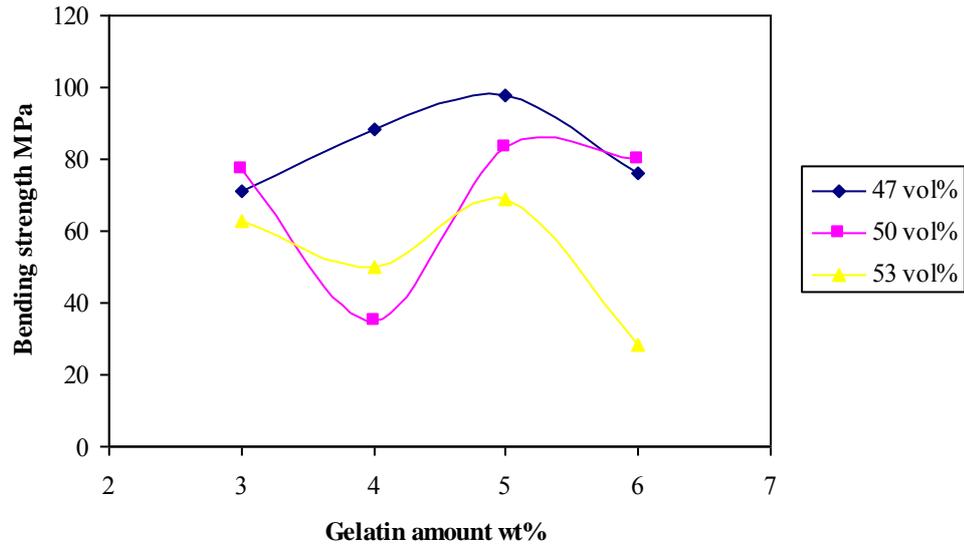


Figure 36. The graphs of change in bending strength of sintered alumina samples due to their gelatin amounts

According to the graph in Figure 35, it's seen a general tendency of increasing in bending strength of the green alumina samples until 5 wt% of gelatin amount, as the gelatin amount increases. After that a sharp decrease in bending strength occurs. 5 wt% of gelatin amount is seen as an optimum point in the graph like it's been in compressive strength due to gelatin amount graphs. Again the effect of alumina solid loading to green body seems uncertain. However, the results match the compressive strength results. Bending strength values of gelcasted green samples with 47 vol% of solid loading are again below those of others before sintering. Then by the effect of sintering their bending strength values increase above those of the others. Maximum bending strength of green samples seems between 3-3.5 MPa. In the study of A. J. Millan et al. maximum bending strength for gelatin-gelcasted alumina is found as 4 MPa [13].

The bending strength graph of sintered alumina bars in the Figure 36 also supports the previous graph. Same increasing tendency until 5 wt% of gelatin amount and then decreasing can be seen in the graph. Maximum bending strength value for sintered alumina samples is 98.05 MPa and belongs to the ceramic body with 47 vol% of alumina content and 5 wt% of gelatin amount. This founding and being 5 wt% gelatin amount an optimum point in bending strength of green and sintered samples match with the founding in the study of Y. Chen et al. that says that a suitable gelatin content for suspensions of 50±53 vol% alumina powder is 4±5 wt% (based on water)

[29]. However, their result about bending strength is very different. It is maximum 304.5 MPa for sintered alumina samples.

CHAPTER 4

CONCLUSIONS

Alumina ceramic samples for mechanical tests were obtained by gelcasting and slip casting. Two kinds of gel former were used. The effects of gelatin and carrageenan gum on mechanical properties of alumina ceramics were investigated. For this purpose bending strength, compressive strength and hardness number of the samples were found as a result of applied mechanical tests. Furthermore, their densification percentages were calculated.

In conclusion, it is seen an optimum point in the gelatin amount in which properties increase until that point and then start to decrease in compressive and bending strength properties of gelatin-gelcasted alumina ceramics. This result is the same for both green and sintered state of gelatin–gelcasted alumina ceramics. It is also seen in compressive strength properties of alumina ceramics gelcasted with carrageenan gum. In this way, it can be said that there is a gel limit which the ceramic body will be able to take. Excess amount of gel causes to decrease in strength of ceramic body above this limit. We believe that as the gel leaves the green body out during binder burn-out stage, it forms small porosities in green body. These porosities are removed or closed by sintering. Excess amount gel may cause larger porosities in green body which can't be removed by sintering.

As a result, optimum gelatin amount for compression and bending strength properties of gelcasted alumina ceramics is the same and 5 wt%. Also densification percentages of the gelatin-gelcasted alumina ceramics after sintering support this founding. Densification percentages also decrease after 5 wt%. of gelatin amount. Maximum compressive and bending strength for gelatin-gelcasted alumina ceramics are 167 MPa and 98.05 MPa respectively.

Optimum gel amount for compression strength property of gum-gelcasted alumina ceramics was found as 1.7 wt% All gum-gelcasted alumina ceramics prepared with 47, 50, 53 vol% of alumina contents show the same behavior. Their compressive strength decreases after 1.7 wt% of gum amount. Gelatin-gelcasted green alumina ceramics are harder than gum-gelcasted green ones. The hardness numbers of gelatin-gelcasted ones change between 90 HV and 145 HV, also that of gum-gelcasted ones

change between 35 HV and 85 HV. We aren't able to set any relation between gel amount and hardness.

At green state compressive strength values of gum-gelcasted alumina ceramics are very smaller than that of gelatin-gelcasted ones. After sintering, they become greater than that of gelatin-gelcasted ones. Maximum compressive strength for gum-gelcasted alumina ceramics is 347.43 MPa. The reason of this situation may be that, carrageenan gum forms much more but smaller pores than gelatin does during binder burn-out stage. Thus, after sintering small pores are closed much easier and gum-gelcasted alumina ceramics include less porosity than gelatin-gelcasted one does. As a result, gum-gelcasted alumina ceramic becomes stronger than the other after sintering.

In the results of compressive and bending strength tests, the strength increasing effects of gelatin and carrageenan gum are seen after they were added in production of alumina ceramics. They have significant contribution on strength of alumina ceramics. In my opinion their strength increasing mechanism can be explained as follows: As a result of leaving the gel out from ceramic body in binder-burnout stage, little pores are formed in microstructure but, these pores are eliminated by sintering. Furthermore, during drying of gelcasted green ceramic, gel adsorbed around the particles loses water. Gel shrinks and makes particles close to each other. Thus, it contributes the particle packaging.

Gelcasting is a useful ceramic forming method for making complex shapes since additive gel gives the casting slip flowability and provides packaging of particles during drying. Consequently, gel provides to increase the densification ratio of final product resulting in high strength.

Gelatin and carrageenan gum are useful gel formers for gelcasting application of ceramics. Furthermore, they are environmentally friendly.

REFERENCES

- 1) Mark A. Janney, Stephen D. Nunn, Claudia A. Walls, Ogbemi O. Omatete, Randy B. Ogle, Glen H. Kirby, and April D. McMillan, Gelcasting, THE HANDBOOK OF CERAMIC ENGINEERING (1998).
- 2) Noah O. Shanti, David B. Hovis, Michelle E. Seitz, John K. Montgomery, Donald M. Baskin and Katherine T. Faber, Ceramic Laminates by Gelcasting, Int. J. Appl. Ceram. Technol., 6 [5] 593–606 (2009).
- 3) Ogbemi O. Omatete, Mark A. Janney & Stephen D. Nunn, Gelcasting: From Laboratory Development Toward Industrial Production, (1997).
- 4) Juanli Yu, Jinlong Yang , Yong Huang, The transformation mechanism from suspension to green body and the development of colloidal forming, Ceramic International (2010).
- 5) R. Gilissen, J.P. Erauw, A. Smolders, E. Vanswijgenhoven, J. Luyten, Gelcasting, a near net shape technique, Materials and Design 259-263 (2009)
- 6) S. Dahara, R. K. Kamboj, M. Pradhan and P. Bhargava, Shape forming of ceramics via gelcasting of aqueous particulate slurries, Bull. Mater. Sci., Vol. 25, No. 6, November 2002, pp. 565–568.
- 7) Jianfeng Xue, Manjiang Dong, Jun Li, Guohong Zhou, Shiwei Wang, Gelcasting of Aluminum Nitride Ceramics, Journal of the American Ceramic Society Volume 93, Issue 4, pages 928–930, April 2010.
- 8) Chunhua Zhang, Xiang Huang, Yansheng Yin, Fengjie Xia, Jinhui Dai, Zhibin Zhu, Preparation of boron carbide–aluminum composites by non-aqueous gelcasting, Ceramics International (August 2009), 35 (6), pg. 2255-2259 .
- 9) Shyama Prasad Mohanty, Processing of BiFeO₃ Ceramics by Gelcasting, Master of Thesis, Department of Ceramic Engineering, National Institute of Technology, Rourkela.
- 10) S. Ananthakumar, K. Prabhakaran , U.S. Hareesh, P. Manohar, K.G.K. Warriar, Gel casting process for Al₂O₃–SiC nanocomposites and its creep characteristics, Materials Chemistry and Physics 85 (2004) 151–157.
- 11) Juanli Yu, Hongjie Wang,, Jian Zhang, Neural network modeling and analysis of

- gel casting preparation of porous Si₃N₄ ceramics, *Ceramics International* 35 (2009) 2943–2950.
- 12) A.J. Millan, M.I. Nieto, R. Moreno, Near-net shaping of aqueous alumina slurries using carrageenan, *Journal of the European Ceramic Society* 22 (2002) 297–303.
 - 13) Arnaldo J. Millan, Maria Isabel Nieto, Carmen Baudin, Rodrigo Moreno, Thermogelling polysaccharides for aqueous gelcasting—part II: influence of gelling additives on rheological properties and gelcasting of alumina, *Journal of the European Ceramic Society* 22 (2002) 2217–2222.
 - 14) James Reed, “Ceramic Processing” book.
 - 15) Ward, A.G.; Courts, A. (1977). *The Science and Technology of Gelatin*. New York: Academic Press.
 - 16) Young Seon Choi, Sung Ran Hong, Young Moo Lee, Kang Won Song, Moon Hyang Park, Young Soo Nam, Study on gelatin-containing artificial skin: I. Preparation and characteristics of novel gelatin-alginate sponge.
 - 17) *Handbook of Food Science, Technology, And Engineering* Y.H.Hui et. al. Yiu H. Hui (2006).
 - 18) *FAO Agar and Carrageenan Manual*. Fao.org (1965-01-01). Retrieved on 2011-12-10.
 - 19) “ Alumina (Aluminium Oxide)- The Different Types of Commercially Available Grades “. *The A to Z of Materials*. <http://www.azom.com/details.asp> Retrieved 2007-10-27. (accessed on 15.12.2012)
 - 20) Patnaik (2002). *Handbook of Inorganic Chemicals*. McGraw-Hill.
 - 21) Isabel Santacruz, Ma Isabel Nieto, Rodrigo Moreno, Alumina bodies with near-to-theoretical density by aqueous gelcasting using concentrated agarose solutions, *Ceramics International* 31 (2005) 439–445.
 - 22) Erik Adolfssonw, Gelcasting of Zirconia Using Agarose, *J. Am. Ceram. Soc.*, 89 [6] 1897–1902 (2006).
 - 23) Murat Bengisu, Elvan Yilmaz, Gelcasting of alumina and zirconia using chitosan gels, *Ceramics International* 28 (2002) 431–438.
 - 24) Santanu Dhara and Parag Bhargava, Egg White as an Environmentally Friendly

Low-Cost Binder for Gelcasting of Ceramics, *J. Am. Ceram. Soc.*, 84 [12] 3048–50 (2001).

- 25) Zhiyong Yu, Yong Huang, Chang-an Wang, Shixi Ouyang, A novel gel tape casting process based on gelation of sodium alginate, *Ceramics International* 30 (2004) 503–507.
- 26) ASTM C1116-94 Standard Test Method for Flexural Strength of Advanced Ceramics at Ambient Temperature.
- 27) ASTM C773-88 Standard Test Method for Compressive (Crushing) Strength of Fired Whiteware Materials.
- 28) L.J. Vandeperre, A.M. De Wilde, J. Luyten, Gelatin gelcasting of ceramic components, *Journal of Materials Processing Technology* 135 (2003) 312–316.
- 29) Yali Chen, Zhipeng Xie, Jinlong Yang and Yong Huang, Alumina Casting Based on Gelation of Gelatine, *Journal of the European Ceramic Society* 19 (1999) 271-275.
- 30) <http://accuratus.com/alumox.html> (accessed on 17.12.2012)

APPENDIX A

AMOUNTS OF THE MATERIALS USED IN GELCASTING SLIP PREPARATION

Table 1. Amounts of the materials in gelcasting slips with gelatin

| Samples | | Alumina suspension | | Gel former solution | | Dispersant (Dolapix) | | | | | | |
|---------------------|--------------------|--------------------|------------|---------------------|------------|----------------------|------|----|-------------|------|-----|-------------|
| Solids loading vol% | Gelatin amount wt% | Alumina (g) | Water (ml) | Gelatin (g) | Water (ml) | | | | | | | |
| 47 | 3 | 250 | 50 | 2.19 | 20.83 | 42-43 drops | | | | | | |
| | 4 | | | 2.95 | | | | | | | | |
| | 5 | | | 3.71 | | | | | | | | |
| | 6 | | | 4.47 | | | | | | | | |
| 50 | 3 | | | 250 | 50 | | 1.92 | 12 | 42-43 drops | | | |
| | 4 | | | | | | 2.55 | | | | | |
| | 5 | | | | | | 3.18 | | | | | |
| | 6 | | | | | | 3.82 | | | | | |
| 53 | 3 | | | | | | 250 | 50 | | 1.72 | 5.7 | 42-43 drops |
| | 4 | | | | | | | | | 2.32 | | |
| | 5 | | | | | | | | | 2.92 | | |
| | 6 | | | | | | | | | 3.52 | | |

Table 2. Amounts of the materials in gelcasting slips with carra. Gum

| Samples | | Alumina suspension | | Gel former solution | | Dispersant (Dolapix) | | | | | | |
|---------------------|-----------------------|--------------------|------------|---------------------|------------|----------------------|------|----|-------------|------|-----|-------------|
| Solids loading vol% | Carra. gum amount wt% | Alumina (g) | Water (ml) | Carra. Gum (g) | Water (ml) | | | | | | | |
| 47 | 1 | 250 | 50 | 0.71 | 20.83 | 42-43 drops | | | | | | |
| | 1.4 | | | 1 | | | | | | | | |
| | 1.7 | | | 1.22 | | | | | | | | |
| | 2 | | | 1.45 | | | | | | | | |
| 50 | 1 | | | 250 | 50 | | 0.62 | 12 | 42-43 drops | | | |
| | 1.4 | | | | | | 0.88 | | | | | |
| | 1.7 | | | | | | 1.07 | | | | | |
| | 2 | | | | | | 1.27 | | | | | |
| 53 | 1 | | | | | | 250 | 50 | | 0.56 | 5.7 | 42-43 drops |
| | 1.4 | | | | | | | | | 0.79 | | |
| | 1.7 | | | | | | | | | 0.96 | | |
| | 2 | | | | | | | | | 1.16 | | |

APPENDIX B

EXPERIMENTAL DATA OBTAINED FROM SOME MEASUREMENTS AND MECHANICAL TESTS

Table 1. Density Measurement Data Table for Gelatin-Gelcast Sintered Samples

| Samples | | Dry weight (g) | | | Weight in air (g) | | | Weight in water (g) | | | Density (g/cm ³) | | | Ave. Density (g/cm ³) | Density TD% | Std. | Density (g/cm ³) |
|--------------------|--------------------|----------------|------|------|-------------------|------|------|---------------------|------|-------|------------------------------|------|------|-----------------------------------|-------------|-------|------------------------------|
| Solid loading vol% | Gelatin amount wt% | 1 | 2 | 3 | 1 | 2 | 3 | 1 | 2 | 3 | 1 | 2 | 3 | | | | |
| 47 | 3 | 2.43 | 2.46 | 2.19 | 2.43 | 2.46 | 2.21 | 1.79 | 1.8 | 1.62 | 3.79 | 3.72 | 3.71 | 3.74 | 94.1 | 0.044 | 3.74±0.044 |
| | 4 | 2.29 | 2.48 | 1.89 | 2.296 | 2.49 | 1.9 | 1.697 | 1.84 | 1.397 | 3.82 | 3.81 | 3.75 | 3.79 | 95.44 | 0.038 | 3.79±0.038 |
| | 5 | 2.12 | 2.25 | 2.25 | 2.15 | 2.26 | 2.26 | 1.56 | 1.65 | 1.66 | 3.59 | 3.68 | 3.75 | 3.67 | 92.39 | 0.08 | 3.67±0.080 |
| | 6 | 2.43 | 2.54 | 2.3 | 2.44 | 2.56 | 2.31 | 1.78 | 1.86 | 1.69 | 3.68 | 3.62 | 3.7 | 3.67 | 92.29 | 0.042 | 3.67±0.042 |
| 50 | 3 | 1.74 | 2.03 | 1.92 | 1.75 | 2.04 | 1.92 | 1.28 | 1.5 | 1.42 | 3.7 | 3.75 | 3.84 | 3.76 | 94.65 | 0.071 | 3.76±0.070 |
| | 4 | 2.25 | 1.65 | 1.89 | 2.27 | 1.67 | 1.89 | 1.67 | 1.22 | 1.39 | 3.75 | 3.66 | 3.78 | 3.73 | 93.77 | 0.062 | 3.73±0.062 |
| | 5 | 2.35 | 2.14 | 2.22 | 2.36 | 2.14 | 2.22 | 1.74 | 1.58 | 1.64 | 3.79 | 3.82 | 3.82 | 3.81 | 95.8 | 0.017 | 3.81±0.017 |
| | 6 | 1.87 | 1.98 | 1.89 | 1.89 | 1.99 | 1.9 | 1.38 | 1.47 | 1.39 | 3.66 | 3.8 | 3.7 | 3.72 | 93.63 | 0.072 | 3.72±0.072 |
| 53 | 3 | 2.27 | 2.48 | 2.32 | 2.3 | 2.5 | 2.33 | 1.67 | 1.83 | 1.71 | 3.6 | 3.7 | 3.74 | 3.68 | 92.51 | 0.072 | 3.68±0.072 |
| | 4 | 2.57 | 2.83 | 2.9 | 2.58 | 2.85 | 2.92 | 1.87 | 2.06 | 2.11 | 3.61 | 3.58 | 3.58 | 3.59 | 90.3 | 0.017 | 3.59±0.017 |
| | 5 | 2.57 | 2.32 | 2.48 | 2.58 | 2.33 | 2.5 | 1.89 | 1.7 | 1.83 | 3.72 | 3.68 | 3.7 | 3.7 | 93.03 | 0.02 | 3.70±0.02 |
| | 6 | 2.41 | 1.58 | 2.13 | 2.43 | 1.6 | 2.15 | 1.74 | 1.15 | 1.54 | 3.49 | 3.51 | 3.49 | 3.49 | 87.9 | 0.012 | 3.49±0.012 |

Table 2. Hardness Measurement Data Table for Cara. Gum Gelcast Green Samples

| Sample | | L-Ave. length of the diagonal (µm) | | | | | Vickers Hardness Number | | | | | Ave. Vickers Hardness Number | Std | Vickers Hardness (HV) |
|------------------------------|-------------------------------|------------------------------------|-----------|-----------|-----------|-----------|-------------------------|--------|-------|-------|-------|------------------------------|-------|-----------------------|
| Solid loading amount (%vol.) | Carrageenan gum amount (%wt.) | indent. 1 | Indent. 2 | indent. 3 | indent. 4 | indent. 5 | 1 | 2 | 3 | 4 | 5 | | | |
| 47 | 1 | 429.11 | 406.33 | 540.26 | 489.89 | 604.69 | 98.67 | 110.05 | 62.25 | 75.71 | 49.69 | 79.27 | 25.01 | 79.27±25.01 |
| | 1.4 | 654.98 | 687.9 | 792.18 | 770.22 | 709.6 | 42.35 | 38.4 | 28.95 | 30.63 | 36.08 | 35.28 | 5.524 | 35.28±5.52 |
| | 1.7 | 600.67 | 546.88 | 654.85 | 542.17 | 624.64 | 50.36 | 60.75 | 42.37 | 61.81 | 46.57 | 52.37 | 8.617 | 52.37±8.62 |
| | 2 | 473.65 | 590.78 | 565.53 | 627.37 | 429.87 | 80.99 | 52.06 | 56.81 | 46.16 | 98.32 | 66.87 | 22.01 | 66.87±22.01 |
| 50 | 1 | 469.89 | 520.93 | 471.79 | 392.23 | 563.71 | 82.29 | 66.95 | 81.63 | 118.1 | 57.18 | 81.23 | 23.15 | 81.23±23.15 |
| | 1.4 | 494.49 | 464.78 | 545.75 | 568.31 | 495.95 | 74.3 | 84.11 | 61 | 56.25 | 73.87 | 69.91 | 11.21 | 69.91±11.21 |
| | 1.7 | 451.21 | 437.59 | 617.13 | 557.97 | | 89.24 | 94.88 | 47.71 | 58.36 | | 72.55 | 23.06 | 72.55±23.06 |
| | 2 | 615.53 | 579.48 | 640.04 | 557.43 | 642.84 | 47.95 | 54.11 | 44.35 | 58.47 | 43.97 | 49.77 | 6.341 | 49.77±6.34 |
| 53 | 1 | 799.47 | 591.97 | 620.42 | | | 28.43 | 51.85 | 47.2 | | | 42.49 | 12.4 | 42.49±12.40 |
| | 1.4 | 566.28 | 596.49 | 678.12 | 681.14 | 564.03 | 56.66 | 51.07 | 39.51 | 39.16 | 57.11 | 48.7 | 8.877 | 48.7±8.89 |
| | 1.7 | 661.81 | 628.63 | 627.11 | 752.19 | 685.29 | 41.48 | 45.98 | 46.2 | 32.11 | 38.69 | 40.89 | 5.839 | 40.89±5.84 |
| | 2 | 599.83 | 588.51 | 624.99 | 572.48 | 675.31 | 50.5 | 52.46 | 46.51 | 55.44 | | 51.23 | 3.744 | 51.23±3.74 |

Table 3. Bending Strength Data Table for Gelatin-Gelcast Green Samples

| Green samples | | Edge a ave. (mm) | Edge b ave. (mm) | F (N) | | | | | Bending Strength (MPa) | | | | | Bending strength ave. (MPa) | Std | Bending strength (Mpa) |
|--------------------|--------------------|------------------|------------------|-------|------|------|-------|------|------------------------|------|------|------|------|-----------------------------|------|------------------------|
| Solid loading vol% | Gelatin amount wt% | | | 1 | 2 | 3 | 4 | 5 | 1 | 2 | 3 | 4 | 5 | | | |
| 47 | 3 | 4.61 | 3.57 | 4.29 | 3.53 | 3.29 | --- | --- | 2.19 | 1.8 | 1.67 | | | 1.89 | 0.27 | 1.89±0.27 |
| | 4 | 4.74 | 3.68 | 4.96 | 5.82 | 5.34 | 6.2 | 4.63 | 2.31 | 2.71 | 2.49 | 2.89 | 2.16 | 2.51 | 0.29 | 2.51±0.29 |
| | 5 | 4.81 | 3.39 | 5.72 | 5.1 | 5.63 | 5.48 | --- | 3.08 | 2.75 | 3.03 | 2.95 | | 2.95 | 0.15 | 2.95±0.29 |
| | 6 | 4.76 | 3.72 | 2.43 | 0.85 | --- | --- | --- | 1.1 | | | | | 1.1 | | 1.1 |
| | 7 | 5.09 | 3.67 | 9.72 | 7.29 | 8.67 | 11.82 | --- | 4.23 | 3.17 | 3.77 | 5.14 | | 4.08 | 0.83 | 4.08±0.83 |
| | 8 | 5.06 | 3.81 | 5.7 | 4.75 | 6.2 | 10.82 | --- | 2.32 | | 2.52 | 4.41 | | 3.08 | 1.15 | 3.08±1.15 |
| 50 | 3 | 4.88 | 3.25 | 3.29 | 3.29 | 4.15 | 4.53 | 3.67 | 1.9 | 1.9 | 2.4 | 2.62 | 2.12 | 2.19 | 0.32 | 2.19±0.32 |
| | 4 | 4.74 | 3.63 | | 2.96 | | 2.57 | | | 1.41 | | 1.22 | | 1.315 | 0.13 | 1.31±0.13 |
| | 5 | 5.03 | 3.83 | 7.92 | 8.39 | 7.58 | 8.15 | 7.58 | 3.21 | 3.4 | 3.07 | 3.3 | 3.07 | 3.21 | 0.14 | 3.21±0.14 |
| | 6 | 5.09 | 3.74 | 6.82 | 5.34 | 3.29 | 3.43 | 7.06 | 2.87 | 2.24 | 1.38 | 1.44 | 2.97 | 2.18 | 0.76 | 2.18±0.76 |
| | 7 | 5.09 | 3.74 | 3.29 | 4.29 | | | | 1.38 | 1.8 | | | | 1.59 | 0.3 | 1.59±0.29 |
| | 8 | 5.03 | 3.66 | 9.01 | 8.06 | 10.2 | 10.82 | 10.4 | 4 | 3.58 | 4.53 | 4.81 | 4.6 | 4.31 | 0.5 | 4.31±0.50 |
| 53 | 3 | 4.7 | 3.7 | 2.43 | 2.73 | 3.19 | 2.67 | 2.96 | 1.13 | 1.27 | 1.48 | 1.24 | 1.37 | 1.3 | 0.13 | 1.3±0.132 |
| | 4 | 4.79 | 3.51 | 3.67 | 2.67 | 1.57 | 3.77 | 3.55 | 1.85 | 1.35 | | 1.9 | 1.79 | 1.72 | 0.25 | 1.72±0.25 |
| | 5 | 5 | 3.64 | 2 | 4.58 | 4.34 | 4.24 | | | 2.07 | 1.96 | 1.92 | | 1.98 | 0.08 | 1.98±0.07 |
| | 6 | 5 | 3.64 | 0.95 | 2.19 | 0.95 | 1.34 | 0.95 | | 0.99 | 0.43 | 0.6 | | 0.67 | 0.29 | 0.67±0.29 |
| | 7 | 5 | 3.64 | 5.87 | 1 | 1.34 | 3.19 | 1.34 | 2.65 | | | 1.44 | 0.6 | 1.56 | 1.03 | 1.56±1.03 |
| | 8 | 5 | 3.64 | 2.34 | | | | | 1.05 | | | | | 1.05 | | 1.05 |

Table 4. Bending Strength Data Table for Gelatin-Gelcast Sintered Samples

| Sintered samples | | Edge a ave. (mm) | Edge b ave. (mm) | F (N) | | | | | Bending Strength (MPa) | | | | | Bending strength ave. (MPa) | Std | Bending strength (Mpa) |
|--------------------|--------------------|------------------|------------------|-------|------|-------|------|-------|------------------------|------|-------|------|------|-----------------------------|-------|------------------------|
| Solid loading vol% | Gelatin amount wt% | | | 1 | 2 | 3 | 4 | 5 | 1 | 2 | 3 | 4 | 5 | | | |
| 47 | 3 | 4.056 | 2.823 | 54.12 | 81.8 | 82.83 | 87.5 | | 50.2 | 75.9 | 76.84 | 81.1 | | 71.02 | 14.06 | 71.02±14.06 |
| | 4 | 4.056 | 2.823 | 103 | 87.2 | 115.9 | 74.2 | | 95.51 | 80.9 | 107.5 | | | 94.63 | 13.32 | 94.63±13.32 |
| | 5 | 4.023 | 2.833 | 125.4 | 74.2 | 117.1 | | | 116.5 | | 108.8 | | | 112.6 | 5.445 | 112.62±5.44 |
| | 6 | 4.245 | 2.995 | 132.3 | 91.3 | 66.04 | | | 104.2 | 71.9 | | | | 88.09 | 22.85 | 88.09±22.85 |
| | 7 | 4.3 | 3.023 | 106.4 | 82.8 | | | | 81.19 | 63.2 | | | | 72.2 | 12.71 | 72.2±12.71 |
| | 8 | 4.04 | 3.015 | 101.5 | 68.1 | 75 | | | 82.89 | 55.7 | 61.26 | | | 66.6 | 14.38 | 66.6±14.37 |
| 50 | 3 | 3.813 | 2.556 | 61.36 | 68.4 | 69.85 | 56.5 | | 73.85 | 82.3 | 84.06 | 68 | | 77.06 | 7.511 | 77.06±7.51 |
| | 4 | 4.22 | 3.055 | 48.44 | | 44.1 | | | 36.89 | | 33.59 | | | 35.24 | 2.333 | 35.24±2.33 |
| | 5 | 4.17 | 2.96 | 107 | 86.5 | 84.78 | 126 | 101.8 | 87.85 | 71 | 69.61 | 103 | 83.5 | 83.08 | 13.82 | 83.08±13.82 |
| | 6 | 4.31 | 3.073 | 124 | 113 | 88.78 | | | 91.39 | 83.5 | 65.42 | | | 80.11 | 13.32 | 80.11±13.32 |
| | 7 | 3.87 | 3.04 | 79.82 | 62 | | | | 66.95 | 52 | | | | 59.47 | 10.59 | 59.47±10.58 |
| | 8 | 4.03 | 3.18 | 124.4 | 101 | 108.8 | 118 | 123.6 | 91.57 | 74.5 | 80.09 | 86.7 | 91 | 84.77 | 7.341 | 84.77±7.34 |
| 53 | 3 | 4.11 | 2.98 | 99.13 | 74.8 | 74.91 | 56.1 | | 81.48 | 61.4 | 61.57 | | | 68.16 | 11.53 | 68.16±11.53 |
| | 4 | 4.246 | 3.163 | 62.27 | 85.7 | 64.08 | | | 43.96 | 60.5 | 45.23 | | | 49.89 | 9.193 | 49.89±9.19 |
| | 5 | 3.873 | 3.01 | 61.79 | 79.9 | 99.85 | | | 52.82 | 68.3 | 85.35 | | | 68.82 | 16.27 | 68.82±16.27 |
| | 6 | 4.1 | 3.043 | 42.53 | 23.3 | 41.9 | | | 33.59 | 18.4 | 33.1 | | | 28.36 | 8.644 | 28.36±8.64 |
| | 7 | 4.146 | 2.96 | 90.59 | 19.6 | | | | 74.8 | 16.2 | | | | 45.51 | 41.43 | 45.51±41.43 |
| | 8 | 4.34 | 2.92 | 25.51 | | | | | 20.68 | | | | | 20.68 | | 20.68 |