Preparation and Optimization Green Gel Casting Technique for Manufacturing Near-Net-Shape Ceramics Using Genetic Algorithm

Mohammed A. Ahmed Al-dujaili1,*, Imad Ali Al-hydary1 and Montaha Abdalhussien1

1Department of Ceramics Engineering and Building Materials, Faculty of Materials Engineering, University of Babylon, Babylon, Hilla, Babylon, P.O. Box: 4, Iraq

*Corresponding author’s email: adujaili@uobabylon.edu.iq

Abstract. Gel casting technique is a promising technology that has ability to produce near-net shape ceramics via using toxic and non-ecofriendly agents. The current work aim to develop green gel casting technique using water as a solvent, agar as a gelling agent, and the microwave thermal treatment instead of cross linker. 8mol% Yttria stabilized zirconia was selected as a case study to produce near-net shape ceramics. The experimental work involved the preparation of Yttria stabilized zirconia nanoparticles via chemical precipitation method. The effect study of agar ratio, Yttria stabilized zirconia solid loading percent on the physical, mechanical, surface properties of the prepared ceramics and selecting of suitable casting conditions. The study has been found that the microwave thermal treatment develops thermally activated cross linking in the agar aqueous solution leading to higher glass transition temperature for agar. The green combination (agar aqueous solution and microwave treatment) can be used as alternative to (monomer, solvent, cross linker) Companion. Also, using the ultrasonic treatment can effectively eliminate needs for dispersants, also the vacuum de-airing treatment. Yttria stabilized zirconia ceramic with high dimensional accuracy, low surface roughness (Ra=2.81 nm) can be obtained using an agar ratio of (0.4%) and solid loading of (65%). The sample can be moulded with complex shape and the green gel, also the pre-sintered body is machineable. The sintered samples have a porosity of (31%) and compressive strength of (234MPa). Regression analysis and genetic algorithm are showed that the obtained microhardness, compressive strength, and surface roughness are predictable.

Keywords: 8YSZ, Near net shape, Gel casting, Genetic algorithm method

1. Introduction

Near Net Shape (NNS) it is an innovative concept of industrial manufacturing. This technicality mains focus on the parts production, as close as possible to their shape or final contour without need for chipping or grinding operations implementation [1]. NNS’s may reducing or eliminating the need for the finishing the surface like machining or grinding and converts benefits of bottom line that can reduce your cost to two-thirds [2]. The ongoing drive to use easy methods for near shaped advanced ceramic components in almost a grid shape has led to a revolutionary class of forming techniques known for its wet processing techniques [3]. GC is referred to as one of the common performing techniques developed to date for fabricating complex-shaped ceramic bodies from highly concentrated and low-
viscosity slurries that can be solidified with gelation once the mold is filled. So; Facilitate mold removal before drying and sintering [4].

Monomer, catalyst, dispersant, solvent, binder, plasticizer, cross linker, and powder of ceramic in gel casting method are mixed thoroughly to produce a high solid loading and low viscosity homogenous suspension [5]. The current work is an attempt to develop green gel casting method that has an ability to manufacture near net shape ceramic. Yttria stabilized zirconia was chosen as a case study to obtain the work. The prediction process was defined as the process of detecting the next steps or results on the basis of any proof or confirmation of these steps [6]. Regression is one of the statistical techniques for the determining of linear relationship between more than one variable. Regression is primarily used for the prediction and causal inference [6]. There are many studies that are focused on the employment of the genetic algorithm for optimization of problems, in the turning processes and joining. In addition, it is present in the field of metals. As, for ceramics the GA is not used commonly and has rarely been documented.

The genetic algorithm method starts with a set of randomly generated individuals in a named population[7]. Each individual is called a chromosome, and every chromosome is evaluated using a certain function is called the fitness function. After that, a new population is generated by employing the genetic algorithm operator (selection, crossover and mutation) which replaces the old population with the new one. Algorithm factors (selection, crossover and mutation) which replaces the outdated population with the new one. This operation is repeated until the optimal solution it was received[8].

2. Materials and methods

2.1 Preparation of (8 Yttria stabilized zirconia) Nanoparticles

Yttria stabilized cubic Zirconia Nanoparticles was prepared via the chemical precipitation method through using zirconyl chloride octahydrate and yttrium chloride hexahydrous with concentrated ammonium hydroxide. The suitable amounts of the two chemicals were dissolved into the 10 L of distilled water and magnetically stirred at room temperature for 1hr. 250 ml of ammonia solution (NH₄OH, 25 NH₃%) was then added drop-wise to the reaction mixed solutions up to pH value of 9 to promote sedimentation. The resulting suspension shown in Figure 1 (a) was magnetically stirred at room temperature for another 1hr. The precipitate was separated by high speed refrigerated centrifuge (GL-12, China). The gel like material, shown in Figure 1 (b), was washed with distilled water until the PH value of 7 was obtained at 100˚C for 48hr in the air. Finally, dry powders, shown in Figure 1 (c), drying was performed were grounded in an agate mortar and then calcined in a furnace at temperature 850˚C for 2hr with a heating rate of 8˚C/min. Figure 2 shows the flowchart of the preparation procedure.

Figure 1. The steppes of sample preparation by chemical precipitat
2.2 Preparation of agar gel

Prior to use the agar in gel casting, the main characteristics of the agar gel were identified. These include the gelation temperature and the minimum agar to water ratio. The gelation temperature is necessary to find out the casting temperature of the slurry in the gel casting process, while, the minimum agar to water ratio is important to get green sample that can be safely handled after the gelation. The agar solution has been prepared via dissolving agar powder in distilled water using microwave treatment for 2 min with power of (900 W) and frequency of (2450 MHz). The solution was cooled down to get the gel and dried to obtain the solid agar. After many experiments, the minimum agar to water ratio was found to be 0.4 wt%. This ratio produces gel that can maintain its shape and consistency up on handling. Based on that, the agar to water ratio of (0.4, 0.5, 0.6, 0.7, 0.8) was specified to be used throughout the study.

2.3 Preparation of dense (8YSZ) samples

8YSZ samples were prepared by gel casting method using solid loading percents of (50, 53, 56, 59, 62, 65 wt. %). These percents were calculated based on the weight percent of the 8 Yttria stabilized zirconia powder to the agar solution containing different amount of agar. The upper limit of solid loading was specified, after many experiments, to get castable gel at the specified casting temperature. For preparing the gel casting slurries the agar solution was prepared by dissolving the desired amount of agar in distilled water with the help of microwave treatment for 1 min using power of (900 W) and frequency of (2450 MHz). The solution was then transferred to water bath at 55°C. The desired amount of 8 Yttria stabilized zirconia nano particles was added to the agar solution at 55°C under sonication and mixing with speed of (1600 rpm) for 15 min.

Figure 2. Shows the flow chart of 8YSZ nano particles procedure
After that the slurry was poured in PVC molds and then cooled down to 10°C in refrigerator. The 8 Yttria stabilized zirconia gel as demolded and aged at room temperature for 24hr and dried in a convection oven at 55°C. The green samples calcined and sintered in two steps. The green samples were calcined at 650°C, and then the samples were subjected to pre-sintering at 1100°C. The final sintering was done at 1500°C with 8°C/min and holding time for 2 hr. The experiment population consists of 30 samples as shown in Tables 1, 2, and 3, each sample is considered a chromosome and each chromosome consists of a number of genes. These genes have been represented by input parameters, in the present work. The regression equation or the fitness function was formed, using Minitab 17 software for microhardness (y1), it can be expressed as follows:

\[
y_1 = -3.95 + 0.1432 (X_1) - 1.58 (X_2) - 0.0239 (X_1) (X_2)
\]  

Where: y1: microhardness, x1: solid loading, x2: agar ratio. The obtained regression equation for compression test (y2) can be expressed as follows:

\[
y_2 = 1025 - 27.9 X (1) - 1284 X (2) + 0.315 (X1) (X1) + 902 (X2) (X2) + 2.03 (X1) (\text{constant})
\]

Where: y2: compression, x1: solid loading, x2: agar ratio

![Flow chart of the experimental work](image-url)
Table 1. Regression equations for the roughness of the surface of the sample (Ra)

| Agar ratios | S     | R-sq    | R-sq(adj) | R-sq(pred) | Formulas                                      |
|-------------|-------|---------|-----------|------------|-----------------------------------------------|
| 0.4         | 0.195654 | 98.70%  | 97.83%    | 91.61%     | $f(x) = 46.8 - 1.273 x + 0.00906 x^2$         |
| 0.5         | 0.0399648 | 99.13%  | 98.55%    | 96.36%     | $f(x) = 8.21 - 0.1053 x + 0.000403 x^2$       |
| 0.6         | 0.216105  | 92.91%  | 88.19%    | 52.69%     | $f(x) = 8.5 - 0.095 x - 0.00011 x^2$          |
| 0.7         | 0.162006  | 96.21%  | 93.69%    | 75.83%     | $f(x) = 23.76 - 0.635 x + 0.00456 x^2$        |
| 0.8         | 0.0638663 | 98.60%  | 97.67%    | 93.54%     | $f(x) = 7.09 - 0.069 x - 0.00004 x^2$         |

Table 2. Regression equations for the roughness of the side of the sample (Ra)

| Agar ratios | S     | R-sq    | R-sq(adj) | R-sq(pred) | Formulas                                      |
|-------------|-------|---------|-----------|------------|-----------------------------------------------|
| 0.4         | 0.126837 | 98.82%  | 98.03%    | 87.98%     | $f(x)= 39.99 - 1.126x + 0.00843x^2$           |
| 0.5         | 0.159831 | 96.80%  | 94.67%    | 87.86%     | $f(x) = -11.83 + 0.646 x - 0.00664 x^2$       |
| 0.6         | 0.158672 | 97.14%  | 95.23%    | 90.72%     | $f(x) = 7.70 - 0.012 x - 0.00101 x^2$         |
| 0.7         | 0.456331 | 95.34%  | 92.23%    | 80.52%     | $f(x) = 16.9 - 0.191 x - 0.00081 x^2$         |
| 0.8         | 0.230109 | 98.20%  | 97.00%    | 93.28%     | $f(x) = 9.0 + 0.053 x - 0.00250 x^2$          |

Table 3. The physical properties of 8YSZ ceramic body

| Agar ratio | Solid loading (wt. %) | Bulk density (gm/cm³) | Porosity% | Real porosity (cm³) | Apparent porosity% | Water absorption% |
|------------|-----------------------|-----------------------|-----------|---------------------|--------------------|-------------------|
| 0.4        | 50                    | 3.3342                | 40.23129921 | 0.3844              | 0.3832             | 9.9034            |
|            | 53                    | 3.4221                | 39.37327034 | 0.355               | 0.3739             | 11.5668           |
|            | 56                    | 3.68025               | 37.7602875  | 0.31                | 0.3637             | 10.9918           |
|            | 59                    | 3.7224                | 31.70870472 | 0.2532              | 0.3021             | 8.6439            |
|            | 62                    | 3.8787                | 35.23517052 | 0.2869              | 0.3506             | 9.59154           |
|            | 65                    | 4.09694               | 31.08719579 | 0.26                | 0.3086             | 7.98472           |
| 0.5        | 50                    | 3.0442                | 41.80051874 | 0.2862              | 0.4309             | 12.76009          |
|            | 53                    | 3.1357                | 40.41475384 | 0.2818              | 0.3935             | 11.5375           |
|            | 56                    | 3.1941                | 39.90488845 | 0.2413              | 0.3839             | 10.574            |
|            | 59                    | 3.2893                | 36.85413088 | 0.2911              | 0.3264             | 10.1755           |
|            | 62                    | 3.4278                | 33.74696991 | 0.3501              | 0.3251             | 9.166             |
|            | 65                    | 3.54766               | 36.31452581 | 0.3436              | 0.346              | 9.9818            |
| 0.6        | 50                    | 2.9997                | 41.76988509 | 0.6132              | 0.3951             | 12.9329           |
### 3. Results and discussion

#### 3.1 Result of particle size

Figure 4 shows the particle size distribution of the calcined 8YSCZ nanoparticles were shown in Figure 3. The powder has immoral particle size distribution with main value of the particle size of $D_{50} = 8.631$ μm.

| D50     | 40.65626 | 41.86305732 | 41.6305732 | 41.86305732 | 41.6305732 | 41.86305732 |
|---------|----------|--------------|-------------|--------------|-------------|--------------|
| D10     | 3.1015   | 3.2432       | 3.4274      | 3.5755       | 3.4525      | 3.61977      |
| D50     | 11.5334  | 10.8923      | 11.307      | 12.0453      | 10.1309     | 8.2315       |
| D100    | 0.7      | 0.8          | 0.7         | 0.8          | 0.7         | 0.8          |

![Figure 4](image_url)

**Figure 4.** Show the particle size distribution of the calcined(Y0.08 Zr0.92 O2) powder.
3.2 Result of XRD
Figures 5 and 6 show the x-ray diffraction pattern of 8YSZ sample sintered at 850°C 1300°C, respectively. The diffraction data is in full agreement with JCPDS (00-030-1468). The sharp peaks and the high intensity indicate the high crystallinity of the sample.

![Figure 5. X-ray diffraction analysis of 8YSZ powder calcined at 850°C](image)

![Figure 6. X-ray diffraction analysis of 8YSZ powder calcined at 1300°C.](image)

3.3 Result of SEM
Figure 7 show the SEM micrograph of 8 Yttria stabilized zirconia powder at different magnification. SEM observation indicated that the powder consists of agglomerated particles in the form near to spheres of diameter less than 100nm.
3.4 Result of DSC

Figure 8 shows the results of DSC patterns for agar powder and the agar gel after drying. This test was performed to find out the glass transition temperature (Tg) of the agar and confirm that thermal activation is developed during the microwave heat treatment. The Tg can be found from the endothermic peak below 100°C for agar. It represents the midpoint of that peak. It has been found that the agar powder has Tg of 81.88°C which is comparable to that reported for agar in the literature. The agar gel exhibited a broad endothermic peak at many locations ranging from about (75-84) °C [9], as well as; reported endothermic peaks of three types of agar gel at many locations ranging from (75-90) °C [10]. While the Tg of the dried Agar gel is 93.46°C. The higher Tg value indicates that the choice of the agar crossed linked during the heat treatment due to thermal activation.

Figure 8. DSC analysis for Agar agar type 1(a) Agar powder and (b) Agar gel after drying
3.5 Result of viscosity

Figure 9 shows the results of the cone-on-plate viscosity test for the agar solution. It was observed that there is a change in the profile of viscosity-temperature diagram. This change indicates the transformation of the solution to gel and hence the viscosity increase. However, the change was occurred at temperature 59°C. The pouring temperature was chosen to be 55°C which is accompanied with moderate viscosity value of (17 mpa.s). It is necessary to have high viscosity enough to move the ceramic particles suspended in the gel and, at the same time, low enough to be poured at molds with complex shapes.

![Figure 9. The effect of temperature on the viscosity of Agar gel for heating and cooling.](image)

3.6 Results of physical properties

3.6.1 Drying and firing shrinkage

Figure 10 shows the dependence of drying shrinkage on the solid loading and agar ratio. It has been observed that the drying shrinkage decreased with increased solid loading and decreased agar ratio. On the other hand; when the solid loading increases the friction between the particles increases. This can hinder the settle of the particles during the casting process. Thus, the compaction can be reduced leading to less values of firing shrinkage. The counter balance between these two effects produced the net firing shrinkage. The net firing shrinkage of 8 Yttria stabilized zirconia ceramic body is shown in Figure 11. It can be noticed that, as general trend, the firing shrinkage decreases with increasing the solid loading. This indicates that the friction effect generally dominated. However, many exceptions are here. This may belong to homogenous distribution of the particles.
Figure 10. Drying shrinkage of 8YSZ ceramic samples

Figure 11. Firing shrinkage of 8YSZ ceramic samples sintered at 1500°C

3.6.2 Result of porosity.

Figures 12 and 13 show that the apparent porosity and real porosity decrease along with increasing solid loading. This is because of two reasons. The first is whenever more quantity of powder is added; the area of contact between the powder particles is considerably increased. Subsequently, the increase in the contact will increase compaction between the particles and this decrease the pore size. The second reason is related to the ratio of agar. The higher ratio of agar leads to higher porosity due to the higher volume left behind the agar during the heat treatment. Also, the affect is analogue to that noticed for apparent porosity. These two properties influenced similarity by the same factors and similar to water absorption results as shown in Figure 14.

Figure 12. Shows the effect of solid loading and agar ratio on apparent porosity of 8YSZ ceramic

Figure 13. The effect of solid loading and agar ratio on the real porosity of 8YSZ ceramic
Figure 14. Shows the effect of solid loading and agar ratio on water absorption of 8YSZ ceramic

3.6.3 Green and bulk density.
Figures 15 and 16 show the increment in density as the solid loading increase for green and bulk density. Also, the density increase when lower amount of agar is used. This is because of the interlink between the atoms, resulting in an increases in efficient compactness, packing and change dimensionality in the 8 Yttria stabilized zirconia structure. The increase in density is ascribed to the reduction in average interatomic spacing in the 8 Yttria stabilized zirconia structure during the heat treatments.

Figure 15. The effect of solid loading and agar ratio on the green density of 8YSZ ceramic

Figure 16. The effect of solid loading and agar ratio on the bulk density of 8YSZ ceramic

3.7 Result of compressive strength
Figure 17 shows that with increasing solid loading content from 50 to 65wt % leads to increase the compressive strength from 34 to 234 Mpa. Also, decreasing agar ratio increases the compressive strength
especially at high solid loading. The enhancement of the compressive strength is related to the reduction of porosity that leads to improvement in the density and compression strength as well.

![Figure 17. The effect of solid loading and agar ratio on the compression strength of 8YSZ ceramic](image)

3.8 Results of near net shape testing

3.8.1 Mechanical profile.

Figures 18, 19, 20, 21, and 22 showed the roughness values of the prepared samples using Ra and Rz measurements. The roughness was tested for the free surfaces (upper surface of the sample) as well as the interface between the sample and the mold (side). It can be noticed that the roughness, for the surface and the side, decreases with increasing the solid loading for specific agar ratio. This is due to the reduction of porosity which affects the roughness in this level. However, it has been observed that the roughness decreases by increasing agar ratio. This is might be due to the higher dispersion of 8 Yttria stabilized zirconia nano particles when high ratio of agar is used. It is important to note that:

1- The Rz roughness measurement is more sensitive to the solid loading than the Ra measurement.
2- The effect the mold material of the surface roughness is obtained at high agar ratio. The roughness of (side) is higher than that of the (surface) when the agar ratio is higher than 0.6%.
Figure 18. Surface roughness Ra and Rz of 8YSZ samples prepared by gel casting in the agar ratio of 0.4 wt%.

Figure 19. Surface roughness Ra and Rz of 8YSZ samples prepared by gel casting in agar ratio of 0.5 wt%.

Figure 20. Surface roughness Ra and Rz of 8YSZ samples prepared by gel casting in the agar ratio of 0.6 %

Figure 21. Surface roughness Ra and Rz of 8YSZ samples prepared by gel casting in agar ratio of 0.7 wt%
3.8.2 Results of AFM.

Figure 23 Shows surface roughness in nano level obtained by AFM test for a sample with 65% solid loading with different agar ratios. It can be noticed that the roughness increases with increasing agar ratio in the samples as shown in Figure 24. Comprising this result with that obtained for micro level roughness indicates that the removing of agar during the heat treatment creates voids in nano level. Thus; agar is responsible on the nano level roughness while the dispersion of the particles and the sintering process are responsible on the micro level porosity. The AFM images of the surface of 8 Yttria stabilized zirconia samples with different agar ratios are shown in Figure 25. It obvious that increasing the agar ratio.
Figure 23. AFM images for the surface of 8YSZ samples with solid loading 65% and different agar ratio

Figure 24. AFM images for the surface of 8YSZ samples with solid loading 65% and different agar ratio

Figure 25. Nano level roughness of 8YSZ samples prepared by gel casting with solid loading 65wt% and different agar ratios
3.9 Results of the genetic algorithm
The results of a genetic algorithm can be representation as a sketch of the fitness value and the number of the generation, generally as the generation’s progress, the fitness value begins to stabilize, at a certain value that represents the optimum value.

3.10 Results of the GA for optimum microhardness
The GA shows that the best fit for the maximization of the microhardness at a population size of 0.4 agar, is found to be 418HV which is equal to the theoretical hardness of 8YSZ ceramic body. As shown in the Figure 26.

![Figure 26. The generation verses the fitness value for microhardness](image)

3.11 Results of the GA for optimum compressive strength
For the compressive strength, the boundaries were taken as the same as that for the microhardness. As shown in the Figure 27, As well as for roughness and AFM results, as shown in the Figures 28, 29, 30, 31, 32 and 33.

![Figure 27. The generation verses the fitness value for compression test](image)

![Figure 28. The generation verses the fitness value for (Ra) surface](image)
Figure 29. The generation verses the fitness value for (Ra) side

Figure 30. The generation verses the fitness value (Rz) surface

Figure 31. The generation verses the fitness value (Rz) side

Figure 32. The generation verses the fitness value for Ra
4. Conclusions

High crystalline yttria stabilized zirconia with a cubic phase is prepared successfully using the chemical precipitation method. The results displayed that the particle size and the particle size distribution of 8YSZ can be controlled by adjusting the method. The new synthesized, Agar, as natural agent, can be used as a gelling agent in gel casting method without using any toxic or harmful agent. Thermal activation is a appropriate activation process for the agar solution; it can be used effectively rather of the using cross linking agents. Usage of ultrasonic treatment is a possible substitute for the vacuum treatment to accomplish the de-airing step. Increasing the solid loading with decrease agar ratio improves the surface roughness, dimension accuracy, microhardness, and compressive strength, demands the use of extreme values of the processing parameters to obtain highly near net shape ceramics according to the results of the genetic algorithm.

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