Optimization of Manufacturing Titanium-Magnesium alloy for Biomaterial Applications using Grey Relational Analyses

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Abstract. The present paper is focusing on improving the performance of titanium-magnesium alloys prepared by the powder metallurgy technique. These alloys show good biocompatibility and bioactivity, but there is still a demand to study their manufacturing factors. Optimizing the manufacturing process of Ti-Mg alloys increases its expected life. The response selected to evaluate the produced alloys are the hardness, the compressive strength, and the porosity, while the affecting manufacturing parameters are the compacting pressure, sintering time, and magnesium content. Three levels of these parameters were selected to design the experiments based on a standard L9 orthogonal array of the Taguchi method. A Grey relational analysis method was performed to optimize the responses. The obtained experimental results were analyzed using Minitab 16 software at a confidence level of 0.5%. The results indicated that the selected parameters significantly influence the responses of the alloy samples. The optimum level of the affecting parameters was found in a compacting pressure of 760MPa, sintering time of 6hours, and 15wt% of magnesium content.

Keywords. Titanium-magnesium alloy, Biomaterial applications, Grey relational analyses.

1. Introduction
Titanium (Ti) and its alloys are widely used for bone replacement as they have good mechanical, physical, and chemical properties [1]. One of the problems related to the metallic implants in orthopedic surgery is the mismatch of the modulus of elasticity between the bone (0.1–30GPa) and the metallic implants (110GPa) for Ti [2]. These materials' porous structure has increasing interest due to their ability to provide a favorable environment for bone ingrowths and matching the mechanical properties to the surrounding bone, especially elastic modulus and stiffness [3]. Titanium is non-osteointegrative. Insufficient osteointegration of Ti with surrounding bone tissue represents a serious challenge for the implantation [4, 5]. Therefore, it is essential to improve the performance of Ti implants, particularly bone healing efficiency. Magnesium (Mg) and its alloys are good candidates for biodegradable metallic implants [6, 7]. However, when Ti is alloyed with Mg, the resulting Ti–Mg alloys are expected to be quite useful as lightweight metallic biomaterials with good mechanical properties and good corrosion resistance [8]. However, Ti–Mg alloys with high Mg content cannot be prepared by conventional melting processes due to the absence of a solid-solution phase in the phase diagram and the high difference between their melting points.

Many methods are used in the fabrication of porous Ti alloys. Using space holder materials in the powder metallurgy route comes into action with many advantages [9], but these materials may have side effects during the sintering of the green compacts. However, few studies on the effects of the compacting pressure, sintering duration, and the Mg contents on the Ti-Mg alloy's produced porosity.
Therefore, there is still a demand to study the effects of these manufacturing parameters on producing Ti-Mg alloy with higher quality. The present work is focused on efficiently solving this problem by optimizing the affecting parameters based on the grey relational analysis (GRA). Therefore, this work aims to improve titanium-Magnesium alloys' properties (compressive strength, hardness, and porosity) by optimizing the process parameters (compacting pressure, sintering time, and magnesium content) using grey relational analyses.

2. Experiment detail

2.1. Used materials and samples preparation
Titanium-Magnesium alloys were prepared by powder metallurgy technique (P/M). Powder of Titanium with impurities lesser than 0.05wt.%, a particle size of 127.6 μm, and powder of magnesium with impurities lesser than 0.05wt%, and a particle size of 56.14μm were used. Powders of Ti and Mg were mixed for 6 hours via a ball mill type (STGQM-15-2) rotating at 350 rev/min to get the powders particles' perfect and homogenous distribution. Uniaxial compacting was performed via double action steel die on electro-hydraulic press type: (CT340- CT440, USA). Steel die with a diameter of 10mm was used to prepare all samples using compacting pressures of (130, 380, and 760MPa). Two types of cylindrical compacted samples had been prepared; one has a 10mm diameter and a 3mm height used for the porosity, the hardness, and the microstructure tests, while the other has a 10mm diameter and a 16mm height used for compression test. Figure (1) shows the sintering procedure performed via an electrical tube furnace with a continued stream of argon gas.

![Figure 1. Sintering procedure of the prepared samples.](image)

2.2. Tests of the specimens

2.2.1. Compression test. Specimens with dimensions of 10mm diameter and 16mm in length were prepared for the compression tests. The tests were carried out based on ASTM (D695 - 85) at room temperature via general testing machine type (WDW 200, No.W1124) and loading of (0.5 mm/min).

2.2.2. Hardness test. The hardness test was carried out according to ASTM E10. The specimens were ground with suitable grinding papers and polished to get a smooth and uniform surface. Brinell's hardness was considered an average of three readings using an indentation ball of 2.5mm- diameter and loading (31.250N).

2.2.3. Porosity test. The porosity of the sintered specimens was measured according to ASTM B-328 as follows [10].

- The weight of dried specimen at 100°C for 6hrs via vacuum furnace with a pressure of 10-4 torr) was recorded and denoted as A.
- At room temperature, the specimen was immersed in oil of density Do = 0.8g/cm3 for 30 minutes, then weighting the impregnated specimen in air. This weight is denoted as B.
- Weighting the fully impregnated specimen in water, this denoted as F.
Use Eq.1 to calculate the porosity (P):

\[ P = \left[ \frac{B-A}{(B-P)}D_0 \right] \times 100 \]

Where: \( D_w = 0.9956\text{g/cm}^3 \), which is the density of water at the ambient temperature (30°C).

2.2.4. **Optical microscope (OM).** The specimens were wet ground with the help of (220, 320, 600, 800, 1000, 1200, 1500, 2000, 2500, and 3000) gravel SiC papers, and then polished using the diamond to get a bright surface. Specimens were etched using the solution consisting of (3ml HF+6ml HNO₃+100 ml H₂O) at room temperature [11, 12]. Distilled water and an electric drier were used to wash and dry the samples.

2.2.5. **X-ray diffraction.** This test was conducted to identify the sintered sample phases under compact pressure 760MPa, sintering time 5hrs and Mg content 25%. Copper target at 40kV and 30mA with a speed of 7°/minutes was used, and a range of 20° = 20 to 80 degrees.

2.3. **The experiments design**

The response selected to evaluate the preparation of the Titanium-Magnesium alloys is the compressive strength, the hardness, and the porosity. These responses are affected significantly by the manufacturing parameters: the compacting pressure, the sintering time, and the magnesium percentage. The experiments were designed based on Taguchi’s L9 orthogonal array via Minitab 16 software. Table (1) shows the affecting parameters and all levels.

| Parameters                  | Notation | Levels         |
|-----------------------------|----------|----------------|
| Compacting pressure (MPa)   | A        | 130 380 760    |
| Sintering time (Hrs)        | B        | 5 5.5 6        |
| Magnesium content (wt%)     | C        | 15 20 25       |

3. **Results and discussion**

Table (2) demonstrates the orthogonal array and the results of the hardness, the compressive strength, and the porosity. It is clear that the hardness is in the range of (23.5-44.5Kg/mm²) while the compressive strength and the porosity were obtained between (30.2-149.3MPa) and (30.3-60.3%) respectively. The required porosity of implant materials is in the range of (20-50%) [9]. Therefore, the resulted range of the porosity of the prepared samples is suitable for biomedical applications. The range of the compressive strength of the prepared samples is higher than that of cancellous bone. This meets the results demonstrated in [9].

| No. | A  | B  | C  | Hardness (Kg/mm²) | Compressive strength (MPa) | Porosity (%) |
|-----|----|----|----|-------------------|---------------------------|--------------|
| 1   | 130| 5  | 15 | 31.8              | 45.8                      | 40.2         |
| 2   | 130| 5.5| 20 | 25.8              | 37.6                      | 50.4         |
| 3   | 130| 6  | 25 | 23.5              | 30.2                      | 60.3         |
| 4   | 380| 5  | 20 | 32.5              | 90                        | 41.7         |
| 5   | 380| 5.5| 25 | 27.8              | 66.8                      | 54.8         |
| 6   | 380| 6  | 15 | 33.9              | 95.7                      | 40.5         |
| 7   | 760| 5  | 25 | 35.4              | 119.9                     | 47.2         |
| 8   | 760| 5.5| 15 | 44.5              | 149.3                     | 30.8         |
| 9   | 760| 6  | 20 | 38.6              | 134.8                     | 44.9         |
Figure (2) shows the influence of the process parameters on the responses through the main effect plots. The figure indicates that the sintering duration has the lowest effect on the responses, while the Mg-contents have the essential influence on the porosity. The compacting pressure has the most considerable influence on the hardness and the compressive strength.

![Main Effects Plot for Means](image)

**Figure 2.** Effect of the process parameters on (a) The Hardness, (b) The Compressive Strength, and (c) The Porosity

4. Optimization by grey relational analyses method

The grey relational analyses (GRA) with the Taguchi method can convert the multi-parametric optimization problem to a single parametric problem. In GRA, the average of the grey relational coefficients (GRCs) for the experiments is calculated. This average corresponding to each response is called grey relational grade (GRG). The higher GRG means that the response is near to the optimum value. The following steps illustrate the grey relational analysis method to determine the controlled parameter's optimal level [13, 14].

**Step 1:** Evaluating each affecting parameter and estimating its quality by calculating the signal to noise (S/N) ratio based on Equation (2), representing the higher-the-better value of the ratio for all selected parameters.

\[
S/N \text{ ratio } (Y_{ij}) = -10 \log_{10} \left( \frac{1}{n} \sum_{k=1}^{n} \frac{1}{y_{ij}} \right)
\]  

Where; (S/N)- Signal to noise ratio, \( y_{ij} \) = observed value of the response, \( i = 1, 2, \ldots n \), \( n \) is the observations number, \( j = 1, 2, \ldots, m \), \( m \) is the responses number (\( m=3 \)).

**Step 2:** Normalizing the ratio, in the range between 0 and 1, using the model to maximize the quality characteristics.

\[
X_{ij} = \frac{(Y_{ij}) - \text{Min}(Y_{ij})}{\text{Max}(Y_{ij}) - \text{Min}(Y_{ij})}
\]  

Where; \( X_{ij} \) = normalized value, \( Y_{ij} \) = observed value of the response.
Higher normalized ratios mean a higher performance of the parameter. The best of these results equals one. Table (3) demonstrates the results of all ratios and their normalization.

Table 3. (S/N) Ratios and their normalization of the affecting parameters.

| No. | Hardness Ratio | Porosity Ratio | Compressive Strength Ratio |
|-----|----------------|----------------|---------------------------|
|     | (S/N)          | (S/N)          | (S/N)                     |
| 1   | 29.9           | 0.4716         | 31.8                      |
| 2   | 28.4           | 0.1949         | 33.9                      |
| 3   | 27.3           | 0              | 36.1                      |
| 4   | 30.2           | 0.5078         | 32.8                      |
| 5   | 28.8           | 0.2611         | 34.5                      |
| 6   | 30.8           | 0.6225         | 31.9                      |
| 7   | 31.2           | 0.6904         | 33.3                      |
| 8   | 32.9           | 1              | 30.2                      |
| 9   | 31.6           | 0.7751         | 32.9                      |

Step 3: Computing the deviation as, Δ = 1 – x_ij, where x_ij = Normalized ratio.

Step 4: Grey Relation Coefficient (GRC) for the j\textsuperscript{th} response in the i\textsuperscript{th} experiment expressed as follows:

\[ GRC = \frac{\Delta_{i} - \Delta_{j} + \gamma \Delta_{max}}{\Delta_{j} + \gamma \Delta_{max}} \]  

(4)

Where Δ - deviation of the response; γ is the characteristic factor (mostly selected as 0.5).

Step 5: Determining (GRG) by the following equation:

\[ GRG = \frac{1}{m} \sum_{i=1}^{m} GRG_{i} \]  

(5)

Where m is the number of responses, the most significant value of GRG is near to the product quality for optimum process parameters [14]. This value is ranked as 1, and the others are given decreasing orders. Table (4) contains all results of these calculations. The best characteristics can be noticed for the experiment (8) having the greatest value of GRG [15]. The average of the GRG at each level for each parameter is demonstrated in Table (5). This is performed by grouping the GRGs by factor level for each column in the orthogonal array and estimating their average. For example, the average GRG of factor A at level 1 will be:

\[ GRG_{A1} = \frac{0.432237 + 0.439276 + 0.555556}{3} = 0.475689 \]  

(6)

Table 4. Deviation, sequences, GRC, GRG, and the rank of each experiment.

| No. | Hardness Deviation Sequences | Porosity Deviation Sequences | Compressive Strength Deviation Sequences | GRG | Rank |
|-----|-----------------------------|------------------------------|-----------------------------------------|-----|------|
| 1   | 0.5283                      | 0.4862                       | 0.7249                                  | 0.4023 | 0.4322 | 9   |
| 2   | 0.8051                      | 0.3831                       | 0.3753                                  | 0.8756 | 0.3634 | 8   |
| 3   | 1.3333                      | 0                            | 1                                        | 1.3333 | 0.5555 | 4   |
| 4   | 0.4922                      | 0.5093                       | 0.5490                                  | 0.4766 | 0.3167 | 6   |
| 5   | 0.7389                      | 0.4035                       | 0.2638                                  | 0.6546 | 0.5066 | 7   |
| 6   | 0.3774                      | 0.5698                       | 0.7008                                  | 0.4163 | 0.2911 | 5   |
| 7   | 0.3096                      | 0.6175                       | 0.4729                                  | 0.5139 | 0.1501 | 3   |
| 8   | 0                           | 1                            | 1                                        | 0.3333 | 0      | 1   |
| 9   | 0.2248                      | 0.6897                       | 0.5603                                  | 0.4715 | 0.0673 | 2   |
Table 5. Mean GRG for the affecting parameters.

| Affecting Parameter | Average GRG | Delta (Max-Min) | Rank |
|---------------------|-------------|-----------------|------|
| Level 1             | 0.4756      | 0.6974          |      |
| Level 2             | 0.5295      | 0.2218          | 1    |
| Level 3             | 0.6974      | 0.05919         | 2    |

Table (5) indicates that the optimal parameter level combination during the preparation of Titanium-Magnesium alloys is A3 B3 C1. This means that the optimum values are compacting pressure of 760MPa, sintering time of 6 hours, and magnesium content equal 15wt.%. The delta value, which represents the difference between maximum and minimum GRG average values, indicates the influential factor on the performance characteristics. According to Table (5), compacting pressure (0.2218) has the highest effect, followed by sintering time (0.05919) and Mg content (0.0328). Table (6) shows the results of the confirmation test carried out to validate GRA's results by applying the optimal parameters experimentally. The match between the experimental and predicted results is obvious.

Table 6. Confirmation test.

| No. | Parameter               | Predicted | Experiment | Error % |
|-----|-------------------------|-----------|------------|---------|
| 1   | Hardness (Kg/mm²)       | 44        | 45.3       | 2.9     |
| 2   | Porosity %              | 36        | 35         | 2.8     |
| 3   | Compressive Strength (MPa) | 148     | 149.7      | 1       |

Analysis of variances (ANOVA) identifies the significant parameter affecting the grey relational grade. Table (7) includes the results of the ANOVA. The compacting pressure is the most influential parameter on the characteristics with a contribution percentage of (93.22) followed by Mg content (6.14%) and sintering time (0.0576).

Table 7. The results of the ANOVA.

| Source                      | DF | Seq SS | Adj SS  | Adj MS  | F       | P       | Cont.% |
|-----------------------------|----|--------|---------|---------|---------|---------|--------|
| Compaction pressure (MPa)   | 2  | 14064.2| 14064.2 | 7032.09 | 160.68  | 0.006   | 93.22  |
| Sintering duration (Hours)  | 2  | 8.7    | 8.7     | 4.33    | 0.10    | 0.910   | 0.0576 |
| Mg Content (wt.%)           | 2  | 926.4  | 926.4   | 463.22  | 10.58   | 0.086   | 6.140  |
| Residual Error              | 2  | 87.5   | 87.5    | 43.76   | 0.5799  |         |        |
| Total                       | 8  | 15086.8|         |         |         |         | 100    |

SS: the sum of squares, DOF: degrees of freedom, MS: Mean Square, Cont.%: contribution percentage (ss parameter/ss total) The results indicated that higher compacting pressure is preferable during the manufacturing of titanium–magnesium alloys. The compressive strength of Ti–Mg alloy decreases with the Mg content. The higher magnesium content means an increase in the pores, which in turn reduces the compressive strength.

5. Optical microscope analyses

Figure (3) shows the specimen's microstructure prepared according to the optimum values of the affecting process parameters. It is clear that the phrase that appeared is the α-Ti phase of the bright color and either pores or magnesium of dark color. Pure Mg may form from the supersaturated Ti matrix due to the equilibrium precipitation during sintering at high temperatures.
Figure 3. The microstructure of sample alloys 15% Mg, 760 MPa is compacting pressure, and 6Hrs sintering time (A): at (100x) mag., and (B): at (200x) mag.

6. X-Ray fluorescence (XRF) test
An X-ray diffraction test was done for the sample. The target used in the X-ray tube was Cu, wavelength =1.542 Å, voltage and current were 30kV and 1.5mA, scanning speed 2deg/min, for scanning rang of 10°-80°. According to Ti-Mg binary phase diagram, Ti and Mg have no trend to form a compound. The XRD patterns of the Ti-Mg alloy are shown in Figure 4. There are not any compounds produced. The absence of any oxides is attributed to the controlled argon atmosphere used during the sintering process. However, some sort of oxides might be lower than the detectability of the used XRD when they are less than 5% [16-18].

Figure 4. X-ray diffraction patterns of Ti-Mg alloy.

7. Conclusion
Titanium - magnesium alloys were prepared using the powder metallurgy technique based on various values of affecting parameters (compacting pressure, soaking time, and magnesium percentage). Optimization of the process parameters to improve the responses (compressive strength, hardness, and porosity) was performed using grey relational analysis. The following can be concluded:

- The optimal process parameters level for optimum responses was obtained with the compacting pressure of 760 MPa, the sintering time of 6hours, and the magnesium content of 15wt. %.
- The compacting pressure, the sintering time, and the magnesium percentage are the parameters having a significant effect on titanium-magnesium alloys' quality. Compacting pressure has the most substantial effect, followed by magnesium content and sintering time.

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