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Multi-Objective Optimization of Nitriding Factors for SPS-Ti-Al-Zr Alloy utilizing Grey Relational Analysis

Ekhlas K. Zamel^{1*}, Haydar Al-Ethari¹, Ali H. Haleem¹

ABSTRACT

To support the long-term performance of load-bearing orthopedic implants, candidate materials should exhibit high surface hardness, excellent corrosion resistance, enhanced wear resistance, and adequate biocompatibility. In this study, a titanium–aluminum–zirconium (Ti–2Al–2.5Zr) alloy was fabricated by Spark Plasma Sintering (SPS) and subsequently treated by gas nitriding to improve its surface characteristics. Surface modification was carried out by gas nitriding method which is based on the diffusion of nitrogen atoms into the metallic lattice, thus forming a dense nitride layer, which improves hardness, corrosion resistance and wear properties. The effects of nitriding temperature, processing time and gas flow rate on surface hardness, corrosion rate and wear behavior were systematically investigated using Taguchi's L9 orthogonal array. The results confirmed the formation of a thin, dense and adherent nitride layer composed mainly of TiN and Ti₂N, integrated with the porous SPS microstructure. This layer increased surface hardness to 704–1016 Hv reduced corrosion rate to 0.211–4.09 mpy, and improved wear resistance to 5.7×10^{-9} – 7.5×10^{-9} g/cm³. Grey Relational Analysis (GR) identified 1050 °C, 35 min, and 15 cm³/min as the optimum nitriding conditions, while ANOVA showed that nitriding temperature was the most influential factor.

Keywords: Ti–Al–Zr alloy, Spark Plasma Sintering (SPS), Nitriding, Surface hardness, and Orthopedic implants

1. INTRODUCTION

Titanium and alloys are widely utilized in biomedical research and development due to their outstanding biocompatibility, resistance to corrosion and high mechanical behavior. Nevertheless, commercially pure titanium (Cp-Ti) has naturally low hardness and low wear resistance. Moreover, Ti6Al4V alloy, which is widely utilized, has been reported to release aluminum and vanadium ions under physiological conditions, which can be of concern in terms of cytotoxicity and possible allergic reactions especially because of containing vanadium (Shah et al., 2016; Nicholson, 2020). Ti -Al -Zr alloys have gained more and more interest as alternatives in the biomedical field in recent years. Despite the fact that these

alloys still contain aluminum, its level is much lower than Ti6Al4V (e.g. 2 wt.% Al vs. 6 wt.%), and vanadium is totally removed. The decrease in the amount of aluminum, as well as the lack of vanadium, is likely to reduce the biological risks associated with the release of ions, without impacting the sufficient mechanical strength. Moreover, the zirconium (Zr) is also famous with its high biocompatibility and corrosion resistance, which leads to enhanced biological safety and possible long-term stability. This compositional structure offers a trade-off between mechanical stability and biological functionality that Ti–Al–Zr alloys are good candidates to be utilized in the possible biomedical applications, such as orthopedic and dental implants (Gobbi, 2019; Molagic, 2010; Robau-Porrúa et al., 2025). The processing path is a decisive factor of defining the microstructure and the overall performance of titanium alloys. Spark Plasma Sintering (SPS) allows the production of high-density, highly refined microstructure Ti–Al–Zr alloys, which are combined to increase mechanical features and potential of osseointegration. However, surface hardness and wear resistance are critical issues especially in load-bearing applications that are frictional or articulating which requires additional surface modification plans (Munir et al., 2006; Wennerberg & Albrektsson, 2009; Zhang et al., 2018).

In order to overcome these difficulties, gas nitriding has been utilized extensively as a useful and industrially feasible surface modification process to titanium alloys. Gas nitriding has a number of benefits over other surface treatments, including the ability to treat intricate geometries, have a very strong metallurgical bond with the base, comparatively low cost of processing, and applicability to porous or SPS-fabricated structures. The process of gas nitriding is based on the diffusion of nitrogen atoms into the metal lattice to create a layer of titanium nitride (TiN) that is dense and adherent and increases the surface hardness, wear resistance, and corrosion resistance. Therefore, SPS processing and gas nitriding combination is a prospective approach to obtaining Ti–Al–Zr alloys with enhanced surface characteristics and possible long-term mechanical integrity of biomedical use (Gotman & Gutmanas, 2014; Starosvetsky & Gotman, 2001; Teresa Raimondi & Pietrabissa, 2000).

While nitriding is a widely studied surface-engineering approach for conventional titanium and Ti–6Al–4V alloys, much less attention has been paid to systematic optimization of nitriding conditions for Ti–Al–Zr alloys prepared by Spark Plasma Sintering, particularly for biomedical use of Ti–2Al–2.5Zr compositions. Ti–6Al–4V continues to be widely utilized because of its advantageous mechanical features; however, concerns about the release of vanadium and the relatively high aluminum content under physiological conditions have led to the development of alternative titanium alloys with a lower content of potentially harmful alloying elements. In this case Ti–2Al–2.5Zr is a vanadium free composition with much less aluminum, while zirconium gives advantageous biocompatibility and corrosion resistance. However, the surface properties of this alloy need to be improved further as load bearing biomedical components require not only adequate bulk mechanical integrity but also high surface hardness, low wear and good resistance to physiological corrosion.

Thus, the scientific originality of the current work is not in the individual usage of SPS, gas nitriding, Taguchi design and GRA, but in the overall use to maximize the surface performance of SPS-fabricated Ti–2Al–2.5Zr alloy. The investigations were mostly focused on the nitriding impacts on single characteristics or more common titanium alloys in the past, whereas the simultaneous optimization of hardness, wear resistance and corrosion resistance for SPS Ti–2Al–2.5Zr has been seldom studied systematically. Since these reactions are interconnected and may not achieve their optimal levels under the same processing circumstances, an individual evaluation of these responses may lead to an inadequate judgment of the most suited nitriding condition. Thus, the present work employs Taguchi L9 experimental design combined with GRA and ANOVA to quantify the effects of nitriding temperature, treatment time, and nitrogen gas flow rate and to determine a processing condition that maximizes hardness and minimizes wear and corrosion rates. This holistic multi-response optimization offers a processing-property correlation that may be beneficial in the development of Ti–2Al–2.5Zr as a possible surface-engineered material for long-term biomedical applications.

2. METHODOLOGY

Materials and sample preparation

Experiments on nitriding were conducted on previously prepared samples of titanium, aluminum, and zirconium (Ti–Al–Zr) alloy that had been sintered by Spark Plasma Sintering (SPS). The sintering was conducted at 700 °C, with a heating rate of 100 °C/min and a pressure of 30 MPa (Gil et al., 1998). The objective of the present research is to improve the hardness, wear resistance, and corrosion resistance of the alloy.

The nitriding was done in a special-purpose gas nitriding furnace that was situated at the Ministry of Science and Technology in Baghdad, Iraq. The furnace has a vacuum-based system with a high-purity nitrogen gas inlet and a digital control unit which accurately controls the temperature, the rate of gas flow and duration of treatment. Fig. 1 depicts the experimental set up.



Figure 1. The Device Nitriding Process

The samples that had undergone SPS-processing were mechanically polished before nitriding. The samples were then cleaned and then put in the furnace chamber which was then evacuated to a high vacuum state in order to remove any residual oxygen and moisture that might otherwise lead to oxidation during the nitriding process.

After stabilization of the vacuum conditions, a high-purity nitrogen gas (99.99 percent) was added into the chamber at constant flow rates of 5, 10 and 15 L/min with a calibrated mass flow controller. The nitriding was conducted in three chosen temperatures; 750 °C, 850 °C, and 1050 °C with the treatment time of 15, 25, and 35 minutes respectively (Zamel et al., 2026). The choice of these factors was based on the Taguchi method, ANOVA, and the combined use of the GRA and the selected factors was utilized to design the experiment and to optimize the nitriding factors and assess their effect on the surface performance.

The furnace was utilized to maintain the necessary temperature during the treatment with the constant supply of nitrogen gas, which allowed atomic nitrogen to enter the Ti-Al-Zr surface and create hard compound layers composed primarily of TiN and Ti₂N of titanium nitrides. After the completion of every nitriding cycle, heating was turned off, and the samples were left to cool slowly in the presence of nitrogen to avoid oxidation of the surface of the nitride.

The treated samples, after cooling, were taken off and their characteristics were thoroughly characterized, i.e. micro hardness, corrosion rate, and wear rate were measured. The analyses were performed to determine how the nitriding factors affected the mechanical and tribological performance of the SPS-processed Ti-Al-Zr alloy.

Mechanical and physical tests

Hardness test

The hardness test was conducted in ASTM E384. The specimens were ground utilizing the relevant grinding papers and then polished in order to obtain a smooth surface. Vickers hardness was determined by measuring three magnitudes with a diamond pyramid indenter with a 136° angle and a load of 62.5 N.

Linear polarization test

Linear polarization measurements of the fabricated specimens were done utilizing artificial Ringer solution at 37°C to determine the corrosion behavior of the fabricated specimen in physiological-like conditions, as per the ASTM G59. Prior to testing, all specimens were polished to a smooth mirror finish and were made in the size of 10 mm in diameter and 3 mm in height. The electrolyte was then poured into the samples. The open-circuit potential (OCP) was recorded up to 40 minutes and the magnitudes were recorded after every 5 minutes to enable the surface to stabilize to an electrochemical state before polarization.

The electrochemical assessment was conducted in a conventional three electrode set up where the platinum electrode was used as the counter electrode, the saturated calomel electrode (SCE) as the reference electrode and the sample as the working electrode as per

ASTM F746-04. Potentiodynamic polarization curves were carried out and the corrosion potential (E_{corr}) and the corrosion current density (I_{corr}) were determined by Tafel analysis of the anodic and cathodic regions. The applied potential was scanned at a rate of 0.2 mV/s in a window of ± 250 mV around the stabilized OCP and each test took ~14 minutes to complete. The corrosion rate was calculated using Formula 1 (Hiromoto, 2019):

$$\text{Corrosion rate (mpy)} = 0.13 I_{\text{corr}} (\text{EW}) / A \cdot Q \quad (1)$$

Whereas: 0.13 - factor of conversion; I_{corr} - corrosion current density ($\mu\text{A}/\text{cm}^2$); EW - equivalent weight (g); A - area (cm^2); Q - density (g/cm^3); and mpy - corrosion rate (mils per year).

Wear test

The wet wear tests of all titanium alloys under investigation at 37 °C were performed utilizing a Pin-on-Disc Tester (ball-on-disc configuration, MT-400, version 10). The counter face ball was made of zirconia (ZrO_2), characterized by a high Vickers hardness of approximately 1400 HV. The normal loads in the wet wear tests were 10 N for 30 min (Attar et al., 2015). During the tests the friction coefficient (COF) and the sliding time were automatically recorded by the machine. Before starting the tests, all titanium alloys specimens under investigation were weighed utilizing a sensitive balance (± 0.0001). Then after 30 min, the specimen test was weighed utilizing the same balance. The test was done according to ASTM G99 (ASTM-G99, 2017), and the volume loss was calculated utilizing the following formula.

$$\text{Volume loss} = \text{Weight loss (g)} / \rho (\text{g cm}^3) \quad (2)$$

Whereas: Weight loss (g) is the weight loss after 1h. ρ (g/cm^3) is the density of titanium alloy under investigation.

$$\text{Wear rate} = \frac{\Delta W}{(2\pi r t) n} \quad (3)$$

Whereas:

ΔW = weight loss (g or mg)

r = wear track radius (m)

t = total test time (s)

n = sliding speed (m/s)

The tests were carried out in the Department of Metallurgical Engineering / College of Materials Engineering / University of Babylon.

The experiments design

The Titanium–Aluminum–Zirconium alloys were evaluated based on three major responses: surface hardness, corrosion rate and wear rate. Particularly, the processing parameters, i.e., nitriding temperature, nitriding duration of treatment and nitrogen gas flow rate have a substantial influence on these performance characteristics. The experimental design was constructed using Taguchi's L9 orthogonal array in Minitab 16 software. Each trial was performed once without repetition due to experimental limitations. Therefore, the statistical confidence of ANOVA may be restricted. The chosen processing factors and their levels are shown in Table 1. Then the Analysis of Variance (ANOVA) was performed to identify the statistical significance and the relative importance of each processing element on the measured responses. Moreover, GRA was used for the multi-response optimization to find out the optimum nitriding conditions for simultaneous improvement of surface hardness, corrosion resistance and wear resistance. The experimental matrix was built using Taguchi L9 orthogonal array to systematically investigate the effects of nitriding temperature, treatment period and nitrogen gas flow rate on hardness, wear rate and corrosion rate. Each treatment condition was investigated without independent replication due to experimental constraints. The present ANOVA should be treated as a comparative assessment of factor effect and not as inferential evidence. No repeated trials were present; therefore, the experimental variability and the pure error could not be independently estimated, reducing the statistical confidence of the calculated F-statistics and p-magnitudes. Nevertheless, the analysis

reveals valuable insights into the relative contributions and response specific trends of the investigated processing elements in the investigated design space. It is advised for future research to conduct hardness, wear and corrosion tests with minimum three independent repeats for enhancing repeatability and statistical robustness of the optimization system. This will let us compute the mean responses, standard deviations, confidence intervals and a more accurate estimate of the experimental error.

Table 1. Key process factors and their selected levels.

Key process	factors	Levels		
Temperatures °C	T	750	850	1050
Time(min)	t	15	25	35
Gas flow rate(L/min)	Q	5	10	15

X-ray diffraction (XRD) analysis

XRD analysis was carried out on the cylindrical samples with the height of 3 mm and diameter of 10 mm in the XRD Laboratory, Kashan University, Iran. The measurements were made on a Philips PW 1840 diffractometer with Cu-K α radiation ($\lambda = 1.54060 \text{ \AA}$). The operating conditions were 40 kV in accelerating voltage and 30 mA in current; The scanning was performed in the 2θ range of 10° to 80° with scanning rate of $7^\circ/\text{min}$.

Optical microscope (OM)

Wet grinding of the specimens was done with a series of SiC abrasive papers having grit sizes of 220, 320, 600, 800, 1000, 1200, 1500, 2000, 2500 and 3000. After grinding, a step in which a diamond was polished was done to achieve a mirror-like surface. To etch, a mixture of 3 ml HF, 6 ml HNO₃, and 100 ml H₂O was utilized at room temperature (Sellappan et al., 2025). The specimens were etched after which they were rinsed with distilled water and dried with electric dryer.

Scanning Electron Microscope (SEM)

SEM was utilized to study the microstructure of powder metallurgy sintered specimens to determine surface morphology, porosity and phase distribution. The samples were polished, etched and examined utilizing a Mira3 Tescan at the Razi Metallurgical Research Center, Tehran, Iran. Pore architecture and phase morphology were detected, which allowed understanding the impact of processing on material features.

3. RESULTS & DISCUSSION

The L9 orthogonal array and the experimental measured hardness, corrosion rate and wear rate after gas nitriding treatment are shown in Table 2. The surface features were significantly improved and the hardness magnitude was reached at 704-1016 HV and the corrosion rate was decreased to 0.211-4.09 mpy. The wear rate was further decreased considerably to the range of 5.7×10^{-9} - 7.5×10^{-9} mm³/N.m and the corrosion rate was 5.93 mpy as against specimens subjected to spark plasma sintering (SPS), prior to nitriding and with a hardness of around 300 HV, a wear rate of 0.0006 mm³/N.m and a corrosion rate of around 5.93 mpy. The results clearly indicate that gas nitriding has a significant effect on the improvement of the surface hardness, wear and corrosion resistance. The synergistic enhancement of mechanical and electrochemical properties implies that the nitride Ti-Al-Zr alloy has a great potential to be applied in load-bearing biomedical devices, especially in long-term implant systems (Zhang et al., 2023b).

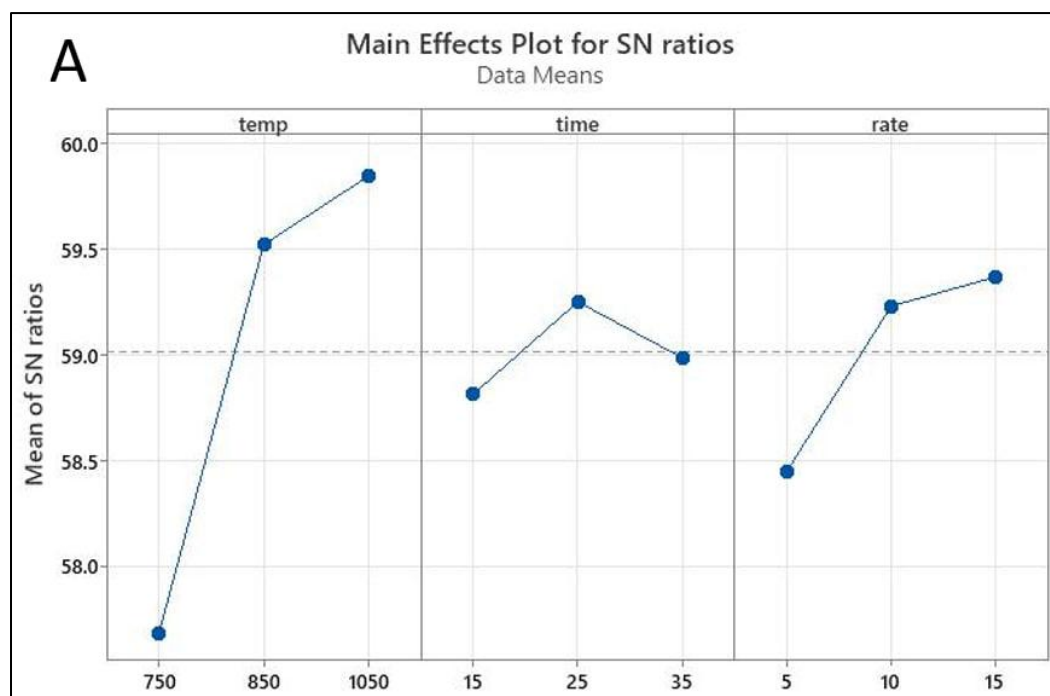
The synergistic effects of nitride-phase development, surface passivation and nitrogen enrichment in the near-surface zone are responsible for the large decrease in corrosion rate after gas nitriding. The XRD revealed the presence of TiN and Ti₂N in the layer, which constitutes a dense physicochemical barrier that prevents direct contact between the Ti-Al-Zr substrate and the surrounding electrolyte, confining the diffusion of hostile ionic species to the metallic matrix. Furthermore, titanium-based surfaces are likely to create a stable passive oxide film, mostly TiO₂, and the nitride layer may improve the protective nature of this surface by limiting the number of electrochemically active sites exposed to the solution. The nitrogen diffusion into the subsurface area may also improve the corrosion resistance by altering the chemical and structural features of the near-surface matrix and decreasing the susceptibility of the alloy to localized electrochemical attack. The combined nitride barrier and passive-film effects are thus predicted to inhibit anodic metal dissolution and to decrease the corrosion current density, in agreement with the reduced corrosion rates recorded after nitriding. Furthermore, the nitride surface might restrict the release of metallic ions to the surrounding environment by reducing direct contact of

the electrolyte with the underlying alloy. However, ion-release measurements and extensive passive-film characterization were not conducted in the current work and therefore these processes should be considered as mechanistically coherent theories rather than directly proven electrochemical events. Additional studies utilizing electrochemical impedance spectroscopy, X-ray photoelectron spectroscopy and ion-release analysis would provide more direct data on passive-film stability, interfacial charge transfer mechanisms and the protective effect of the nitride surface.

Table 2. Influencing factors and the resulting responses

Temperature (°C)	Time (min)	Gas flow rate (L/min)	Hardness [HV]	Wear rate*10 ⁻⁹ (g/cm ³)	Corrosion Rate (mpy)
750	15	5	704	7.1	4.020
750	25	10	796	7.5	3.820
750	35	15	802	7.2	4.090
850	15	10	956	6.4	2.240
850	25	15	1016	7.2	3.700
850	35	5	872	6.4	2.880
1050	15	15	986	6.3	3.050
1050	25	5	954	6.5	0.740
1050	35	10	1007	5.7	0.211

Fig. 2 shows the influence of the processing factors on the responses measured utilizing main effect plots. The analysis reveals that the duration of sintering has the least impact on the responses that are being evaluated, and the rate of flow of nitrogen gas has a significant impact on surface hardness. Conversely, processing tearing nitriding temperature has the strongest effect on all the responses such as hardness, corrosion rate, and wear rate. This strong influence of temperature may be explained by the fact that it directly affects the kinetics of diffusion of nitrogen in the nitriding process. High temperatures increase the rate of diffusion of the nitrogen atoms into the alloy hence increasing the formation and growth of the nitride layer. This causes a greater increase in layer thickness and altered surface composition, all of which enhance hardness, corrosion resistance and wear behavior. On the other hand, other factors like the rate of gas flow and duration of treatment nitriding are the main factors that affect the process indirectly after the temperature driven diffusion process is set.



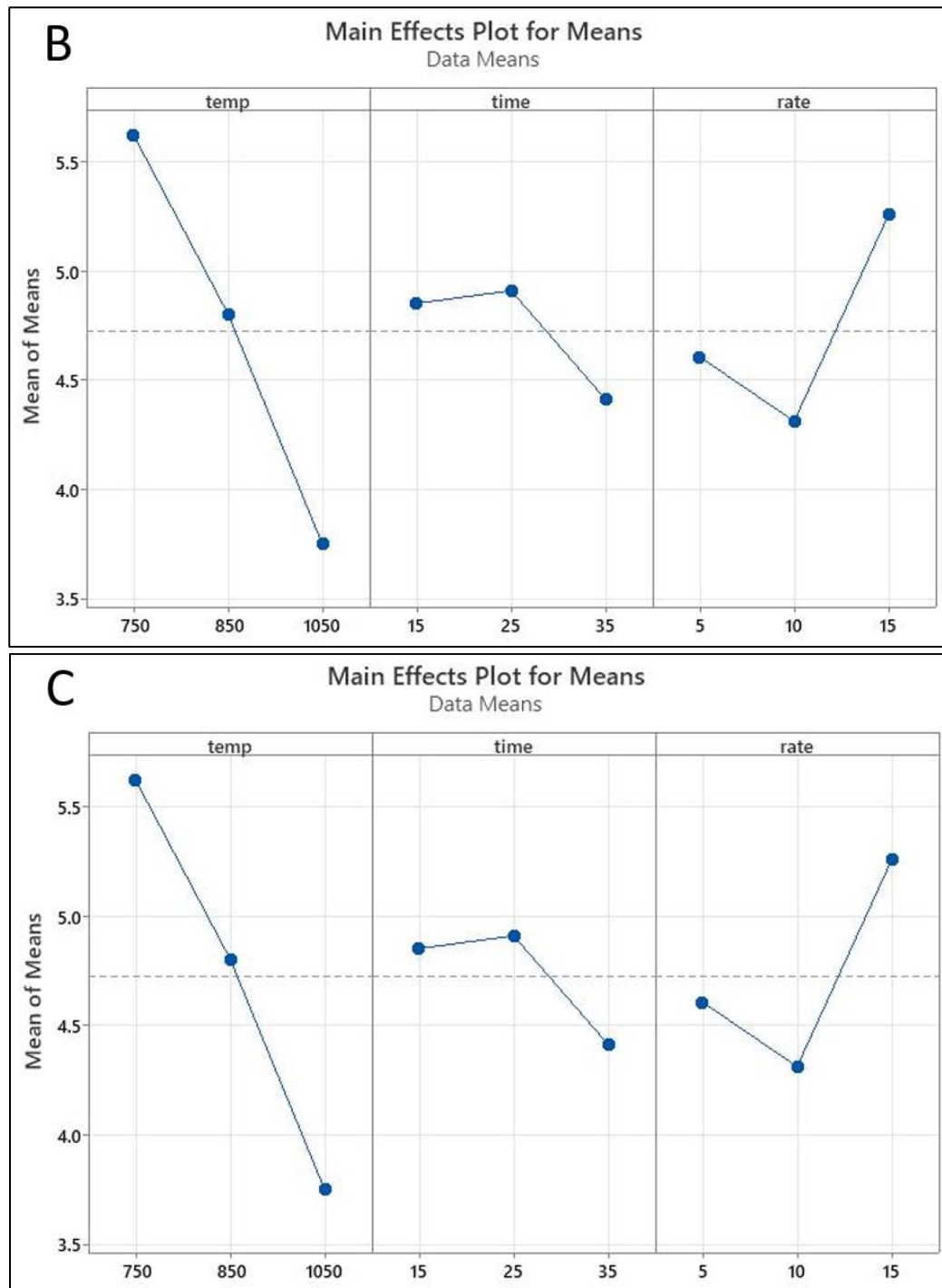


Figure 2. Main effects of processing factors on (A) hardness, (B) corrosion rate, and (C) wear rate

Multi-Response Optimization utilizing the GRA Method

The GRA technique along with Taguchi method provides a systematic and effective framework for solving multi-response optimization problems by converting them into an equivalent single-response optimization model. In this methodology, Gray Relational Coefficient (GRC) is calculated for each experimental run first. The Gray Relational Grade (GRG) is then obtained by averaging the corresponding GRC values of all the performance characteristics evaluated. A higher GRG means the associated experimental condition is closer to the ideal optimal state. The complete GRA-based optimization procedure includes several important stages, which are explained in detail in the relevant publications (Al-Ethari et al., 2021; Julong, 1989).

Step 1: Calculation of the Signal-to-Noise (S/N) Ra

S/N proportion is calculated to evaluate the performance quality of each influencing factor. The selection of the appropriate S/N proportion formulation depends on the desired quality characteristic of the response, such as “larger-the-better,” “smaller-the-better,” or “nominal-the-best.

(a) For “Higher-the-Better” characteristics

$$S/N \text{ ratio}(Y_{ij}) = -10 \log_{10} \left[\left(\frac{1}{n} \right) \left(\sum_{i=1}^n \frac{1}{y_{ij}^2} \right) \right] \quad (4)$$

(b) For “Lower-the-Better” characteristics

$$S/N = -10 \log_{10} \left(\frac{1}{n} \sum_{i=1}^n y_i^2 \right) \quad (5)$$

Whereas; (S/N)- Signal to noise proportion, y_{ij} = detected magnitude of the response, $i = 1, 2, \dots, n$,
 y_i = detected magnitude of the response in the i^{th} experiment, n = number of observations

In this study, the higher-the-better criterion was adopted for hardness, whereas the “lower-the-better” criterion was applied to both wear rate and corrosion rate (C.R.). Accordingly, improved overall performance is associated with increased hardness and reduced wear and corrosion rates.

Step 2: Normalization of S/N proportions

To allow a fair comparison among different response characteristics, the S/N proportions are normalized into a range between 0 and 1.

The normalization model depends on whether the goal is maximization or minimization (Hsiao et al., 2007; Johnson, 2006).

(a) For “Higher-the-Better”

$$X_{ij} = \frac{(Y_{ij}) - \text{Min}(Y_{ij})}{\text{Max}(Y_{ij}) - \text{Min}(Y_{ij})} \quad (6)$$

(b) For “Lower-the-Better”

$$X_{ij} = \frac{\text{Max}(Y_{ij}) - (Y_{ij})}{\text{Max}(Y_{ij}) - \text{Min}(Y_{ij})} \quad (7)$$

Whereas: X_i = normalized magnitude, Y_i = corresponding S/N proportion

Higher normalized magnitudes correspond to better performance, with the optimal normalized magnitude being equal to one. Table 3 presents the results of all calculated proportions along with their normalized magnitudes.

Table 3. S/N proportions and Their Normalized Magnitudes for the Influencing Factors

No.	Hardness (S/N) proportion	Wear rate Normalized (S/N) proportion	Corrosion rate (S/N) proportion
1	56.951	0	-17.025
2	58.018	0.335	-17.501
3	58.083	0.355	-17.146
4	59.609	0.834	-16.123
5	60.137	1	-17.146
6	58.810	0.583	-16.123
7	59.877	0.918	-15.986
8	59.590	0.828	-16.258
9	60.060	0.976	-15.117

Step 3: Calculation of the deviation, Δ , is performed utilizing the formula $\Delta = 1 - x_{ij}$, whereas x_{ij} represents the normalized magnitude of the response.

Step 4: The Grey Relational Coefficient (GRC) for the j^{th} response in the i^{th} experiment is calculated utilizing the following expression:

$$GRC = \frac{\Delta_{min} + \gamma \Delta_{max}}{\Delta + \gamma \Delta_{max}} \quad (8)$$

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

Step 5: Determining (GRG) by the following formula

$$GRG = \frac{1}{m} \sum_{i=1}^m GRG_i \quad (9)$$

Whereas m represents the number of responses, the highest Grey Relational Grade (GRG) corresponds to the optimal process factors that yield the best overall product performance (Al-Ethari et al., 2021). This optimum magnitude is assigned a rank of 1, while the remaining GRG magnitudes are ranked in descending order. The results of these calculations are shown in Table 4 and show that the experiment 9 is the best performance and maximum GRG (Johnson, 2006). Table 5 summarizes the average GRG for each factor at each level. This is done by grouping the GRG magnitudes according to the factor levels of each column of the orthogonal array and taking the average. For example, the mean GRG of factor A at level 1 may be determined as follows:

$$GRG_{AL} = \frac{0.3509 + 0.3670 + 0.3800}{3} \quad (10)$$

Table 4. Deviation, Sequences, Grey Relational Coefficient (GRC), Grey Relational Grade (GRG), and Experimental Ranking

No.	Hardness	Wear rate		Corrosion rate		GRG	Rank	
	Deviation Sequences	GRC	Deviation Sequences	GRC	Deviation Sequences			GRC
1	1	0.333	0.800	0.385	0.994	0.335	0.3509	9
2	0.665	0.429	1	0.333	0.977	0.339	0.3670	8
3	0.645	0.437	0.851	0.370	1	0.333	0.3800	7
4	0.166	0.751	0.422	0.542	0.797	0.386	0.5595	5
5	0	1	0.851	0.370	0.966	0.341	0.5704	4
6	0.417	0.545	0.422	0.542	0.882	0.362	0.4831	6
7	0.082	0.859	0.365	0.578	0.901	0.357	0.5980	3
8	0.172	0.744	0.479	0.511	0.423	0.542	0.5988	2
9	0.024	0.954	0	1	0	1	0.9847	1

Table 5. Average Grey Relational Grade (GRG) for the influencing factors

Affecting Factor	Average GRG			Delta (Max–Min)	Main Effect	Rank
	Level 1	Level 2	Level 3			
T (temp)	0.365975	0.537674	0.727190	0.361215		1
t (time)	0.502801	0.512076	0.615962	0.113161		3
Q (rate)	0.477606	0.637088	0.516145	0.159482		2

Table 5 shows the best processing factors to be utilized in making the Ti -Al -Zr alloy as T3t3Q3, which has the highest temperature (T3), the longest processing time (t3) and the highest rate of gas flow (Q3). The factor set has the highest overall performance, which is indicated by the highest Grey Relational Grade (GRG). The delta (Δ), which is the difference between the highest and lowest average GRG of each of the control factors, indicates the relative impact of each factor on the overall performance characteristics. According to the computed Δ magnitudes, temperature of nitriding (T) has the highest effect, then gas flow rate (Q) and least influence is placed on

processing nitriding time (t). Even though the three factors are important in the improvement of the alloy performance, the temperature is the major one. Therefore, the three factors of maximum nitriding temperature, nitriding time and gas flow rate in the nitriding process constitute the optimum condition of producing high overall features. Moreover, Table 6 shows the outcomes of the validation experiment that was performed to confirm the GRA-based optimization. The fact that there is a close correspondence between the experimentally determined and predicted results proves the effectiveness and reliability of the given optimization approach.

Table 6. Confirmation Experiment

No.	Factor	Predicted	Experiment	Error%
1	Hardness (Hv)	977.8	1007	2.9
2	Wear rate(g/min)	5.54	5.7	2.8
3	Corrosion rate(mpy)	0.209	0.211	1

The relative contribution and the statistical significance of the nitriding factors controlling the overall performance of the Ti–Al–Zr alloy was quantified through Analysis of Variance (ANOVA). From Table 7, it can be seen that the main factor affecting the Gray Relational Grade (GRG) was nitriding temperature. The effect of the other factors was found to be dependent upon the response. Effect of nitrogen gas flow rate was secondary on hardness and corrosion behavior and nitriding duration had relatively bigger effect on wear performance. The difference indicates that the single responses are not equally susceptible to the changes of the processing conditions and therefore cannot be analyzed using a single generalized trend, but a multi-response optimization strategy is needed to achieve a balanced blend of hardness, wear resistance and corrosion resistance (Li et al., 2023; Roliński, 2016). The optimum processing condition determined by the Taguchi–GRA is validated by the confirmation experiment as given in Table 6. The measured hardness, wear rate and corrosion rate magnitudes are 1007 HV, 5.7 and 0.211 mpy, respectively, in comparison to the predicted magnitudes of 977.8 HV, 5.54 and 0.209 mpy. The resulting variances of 2.9 %, 2.8 %, and 1.0 % suggest good agreement between the anticipated and experimental responses and offer a preliminary confirmation of the optimized nitriding setting. However, the present dataset is not sufficient for a rigorous statistical evaluation of repeatability or experimental variability, since only one confirmation experiment was performed. Therefore, replicated confirmation trials are recommended in future work to determine the mean response, standard deviation and confidence intervals, and to improve the reproducibility and statistical robustness of the optimized processing condition.

Table 7. ANOVA Table for Second -order Models for Hardness, corrosion rate and wear rate

ANOVA Table for hardness							
Source	DF	Seq SS	Adj SS	Adi MS	F	p	Cont (%)
Temperature (A)	2	80044.22	80044.22	40022.11	80.78	0.012	81.70 %
Time (B)	2	2538.89	2538.89	1269.44	2.56	0.281	2.59 %
Gas flow rate (C)	2	14393.56	14393.56	7196.78	14.53	0.064	14.69 %
Residual Error	2	990.89	990.89	495.44	–	–	1.01 %
Total	8	97967.56	97967.56	–	–	–	100 %
ANOVA Table for wear rate							
Source	DF	Seq SS	Adj SS	Adi MS	F	P	Cont%
Temperature(A)	2	1.8200	1.8200	0.9100	273.00	0.004	67.10 %
Time(B)	2	0.6467	0.6467	0.3233	97.00	0.010	23.85 %
Gas flow rate(C)	2	0.2067	0.2067	0.1033	31.00	0.031	7.62 %
Residual Error	2	0.0067	0.0067	0.0033	–	–	0.43 %
Total	8	2.6800	2.6800	–	–	–	100 %
ANOVA Table for corrosion rate							
Source	DF	Seq SS	Adj SS	Adi MS	F	P	Cont %
Temperature(A)	2	10.6404	10.6404	5.3202	8.526	0.105	68.36 %
Time(B)	2	0.7555	0.7555	0.3777	0.605	0.61	4.85 %
Gas flow rate(C)	2	3.6655	3.6655	1.8328	2.937	2.94	23.55 %
Residual Error	2	1.2481	1.2481	0.6240	–	–	3.23 %
Total	8	16.3095	16.3095	–	–	–	100 %

The outcome of the ANOVA shows that the hardness, wear rate, and corrosion rate of the Ti–Al–Zr alloy are the most affected variables by the nitriding temperature. Temperature has a statistically significant effect with a high practical contribution of 81.7% ($p = 0.012$). Processing nitriding time, in contrast, does not have any statistical or practical significance ($p = 0.281$, contribution = 2.59%), whereas the nitrogen gas flow rate has a moderate practical contribution (14.69%) but is not statistically significant. All the processing factors are found to be statistically significant in the case of wear rate. The most significant factor is temperature ($p = 0.004$, contribution = 67.10%), then the processing time ($p = 0.010$, contribution = 23.85%), and the gas flow rate has a relatively minor contribution (7.62%) with a borderline significance. In the case of corrosion behavior, temperature once again becomes the most controlling factor with 68.36 percent of the total variation followed by nitrogen gas flow rate (23.55 percent). Processing time has a slight practical impact (4.85%), and it is not statistically significant. In general, these results point to the fact that the accurate regulation of nitriding temperature is the key to the optimization of the mechanical and surface-related characteristics of the Ti–Al–Zr alloy. Although the rate of flow of nitrogen gas can have a second practical impact, processing nitriding time demonstrates a low impact both statistically and practically (Kwak, 2023).

X-Ray Diffraction Analyses

The XRD pattern of the nitride Ti–Al–Zr alloy shows the α -Ti matrix and TiN and Ti₂N phases, which indicate that the gas nitriding resulted in a nitrogen modified surface layer and the titanium-based phase is preserved underneath. The presence of α -Ti reflections implies that the nitriding treatment was mainly restricted to the near surface region without a complete modification of the bulk alloy. The TiN and Ti₂N peaks are indicative of progressive incorporation of nitrogen and formation of nitride. Qualitative indications of differences in phase abundance and surface transformation can be inferred from the relative prominence of the nitride and matrix reflections; however, the present data do not permit a conclusive determination of preferred crystallographic orientation since quantitative peak-intensity analysis and texture coefficients were not determined (Figure 3). Similarly, the crystallite size, lattice strain, crystallinity and residual stress were not quantified since these factors would require additional peak-profile analysis (e.g. Scherrer or Williamson-Hall evaluation) and dedicated residual-stress measurements. However, the phase constitution detected in the present study agrees with previous studies on nitride titanium alloys, whereas TiN and Ti₂N are generally reported as the main nitrogen-containing phases responsible for the increased hardness, wear resistance and corrosion performance of the treated surface (Al-Ethari et al., 2021; Lee et al., 2012; Li et al., 2023). In particular, the formation of TiN has been associated with the formation of a hard and chemically stable surface barrier, while Ti₂N is often considered an intermediate phase related to the nitrogen diffusion below the outer nitride-rich layer.

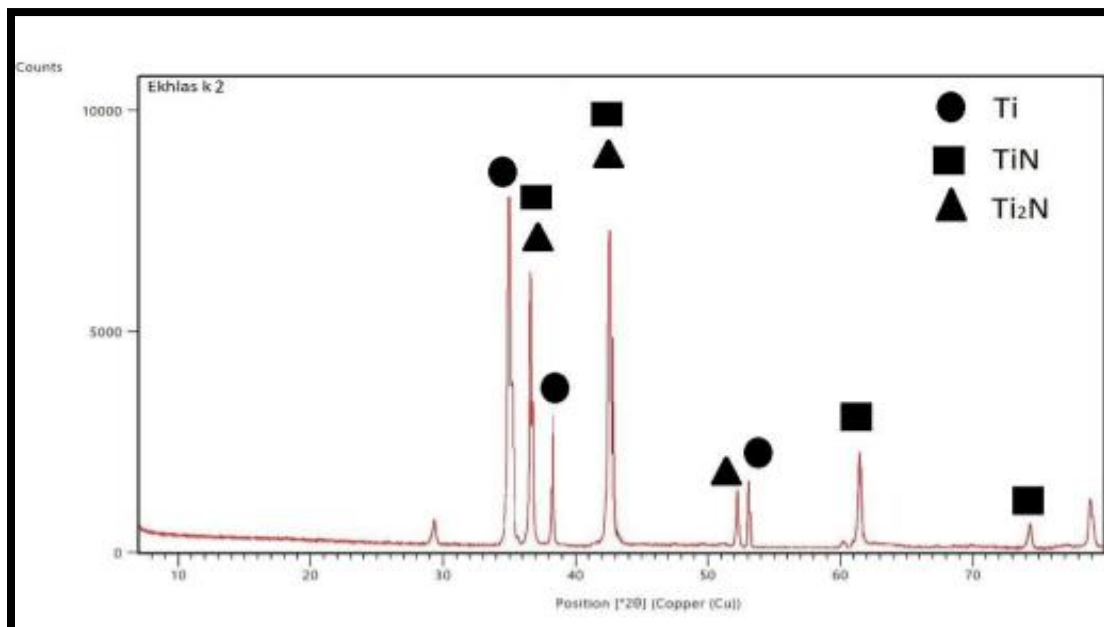


Figure 3. The XRD pattern of the nitride alloy

The diffraction peaks around 35° – 40° and near 53° correspond to the α -Ti phase (HCP), and their persistence after nitriding proves that the treatment is mainly limited to the near-surface region. In contrast, TiN peaks appear around 36° – 37° and 42° – 43° , confirming the high chemical affinity between titanium and nitrogen and the formation of a hard ceramic layer with high hardness and improved wear and corrosion resistance (Lee et al., 2012). Moreover, the appearance of Ti_2N peaks suggests the development of a diffusion-controlled transition zone beneath the TiN layer, resulting in a graded multilayer structure that improves interfacial adhesion and reduces the possibility of delamination during mechanical loading.

Optical Microscope Analyses

Fig. 4 demonstrates the microstructure of the Ti–Al–Zr alloy that was subjected to the best nitriding conditions. The specimen that is subjected to 1050°C at 35 min under a flow rate of 15 L/min of nitrogen gas forms a dense and relatively uniform nitride layer, which is mostly composed of TiN and Ti_2N phases (Almeida et al., 2018). The TiN is credited with the golden-orange areas, and the darker areas are credited to Ti_2N and transitional areas between the nitride surface and the underlying 2-phase titanium matrix of 2-phase titanium. The high nitriding temperature greatly increased the rate of diffusion of nitrogen resulting in coarsening of the grains and the creation of a coating of compound of a higher thickness. The residual porosity that has been left behind by the spark plasma sintering (SPS) process is still visible, but these pores are partially covered by the nitride phases which enhances interfacial continuity between the surface layer and the substrate. These microstructural characteristics can be utilized to improve the surface stability and interfacial performance in the biomedical setting. In general, the gas nitriding treatment is a hardened surface that has enhanced wear and corrosion resistance and does not alter the internal $\alpha + \beta$ microstructure of the alloy. This surface modification and structural integrity imply that the nitride Ti–Al–Zr alloy has a great potential to be utilized as load-bearing biomedical materials (Al-Ethari et al., 2021; Chen et al., 2016; Mogale & Matizamhuka, 2020).

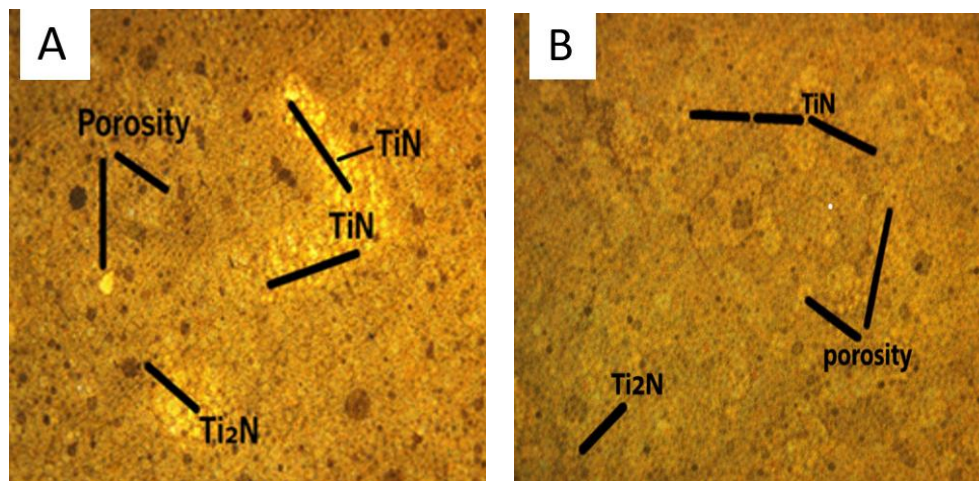


Figure 4. Microstructure of Optimally Processed Alloy Specimens at Different Magnifications: (A) 100 $\times$, (B) 200 $\times$

Scanning Electron Microscopy Study of The Optimal Sample

FESEM imaging of Ti–Al–Zr alloy prepared by Spark Plasma Sintering and nitride at 1050°C showed a dense and uniform surface morphology with insignificant open porosity. The homogeneous contrast of SE mode is a sign of good densification through SPS and the lack of coarse surface features is evidence of a thin continuous layer of nitride. These microstructural characteristics validate that 1050°C offers an optimal compromise between the surface modification and stability. Figure 5 shows FESEM micrograph of the Ti–Al–Zr alloy produced by the Spark Plasma Sintering (SPS) and nitride at 1050°C .

The microstructural development of the gas-nitrided Ti–Al–Zr alloy is due to the combined influence of nitride-phase production, subsurface nitrogen diffusion, the pre-existing SPS microstructure and thermally induced changes in the matrix, rather than being governed simply by TiN formation. The optical micrographs demonstrate a modified near-surface zone and residual porosity inherited from the Spark Plasma Sintering process. XRD results revealed the presence of TiN and Ti_2N following nitriding. The transition from the hardened surface to the base Ti–Al–Zr substrate is expected to be gradual because of the nitrogen-affected diffusion zone below the nitride-rich surface. Interstitially dissolved nitrogen can locally reinforce the titanium matrix and reduce the abrupt mechanical

mismatch between the compound layer and the bulk material. Nitrogen transport during nitriding may occur by lattice diffusion as well as preferred grain boundary channels. Preferred grain boundary channels are higher diffusivity pathways that allow penetration into subterranean locations. Grain expansion or coarsening due to thermally activated atomic mobility at the comparatively high nitriding temperature might potentially lead to changes in grain-boundary density and hence to altered local nitrogen transport and nitride formation. The residual porosity typical of the SPS fabricated alloy also has a significant effect on the nitriding response: open and near-surface pores increase the effective surface area exposed to nitrogen and provide additional penetration routes, resulting in local variations in the nitride layer morphology and diffusion depth; however, excessive porosity can break the continuity of the modified layer and act as a local site of stress concentration. Moreover, the conventional SPS consolidation process results in a metallurgical bonding and neck development between the neighboring powder particles, which improves the interparticle continuity and mechanical integrity. Further diffusion activation in these locations and possible facilitation of local neck formation may occur during subsequent high temperature nitriding, but it was not quantitatively tested in the current work. The observed hardness increase and the improved wear and corrosion resistance should be interpreted as the net effect of the TiN/Ti₂N containing surface region, the nitrogen enriched subsurface diffusion zone, the interparticle bonding formed during SPS, and the competing effects of residual porosity and thermally induced grain evolution. This demonstrates that the surface performance of the nitrided SPS Ti–Al–Zr alloy is dictated by a coupled surface–subsurface microstructural response rather than by the formation of TiN alone.

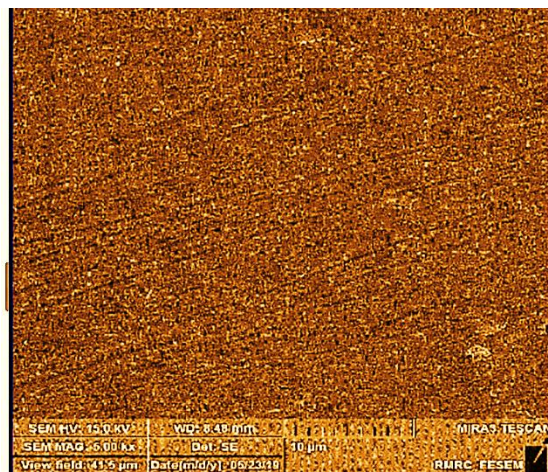


Figure 5. The FESEM micrograph of the Ti–Al–Zr alloy

Cross-Sectional Microscopy for Nitride Layer Measurement

Cross-sectional scanning electron microscopy was utilized to analyze the nitrided zone formed in the Ti–Al–Zr alloy after 1050 °C for 35 min with a gas flow rate of 10. In these circumstances the nitrogen was injected on the surface of the alloy and diffused into the titanium based matrix. This led to a distinct multilayered nitrided area as shown in Figure 6. The outermost area was a complex layer with an average thickness of about 15 μm, which was mainly related to the development of titanium nitride phases, in particular, TiN and Ti₂N. Directly beneath this layer a thin diffusion zone of about 2 μm was detected, bringing the total nitrided depth to almost 17 μm; in this layer nitrogen is thought to be interstitially dissolved in the titanium lattice, leading to the formation of an α-Ti(N) solid solution. Also, a transition area of around 9 μm thickness was found below the diffusion zone, which resulted in a total nitrogen impacted depth of about 26 μm. In the inner area, the nitrogen concentration should fall gradually toward the unaffected substrate, consistent with the diffusion-controlled nature of the nitriding process. These different zones might be mainly due to the high nitriding temperature which increases the nitrogen diffusivity and also the treatment period which gives enough time for the formation of compound-layer and nitrogen diffusion into the subsurface. Nitrogen transport may occur across the titanium crystal lattice as well as grain boundaries whereas these may serve as favorable high-diffusivity paths for deeper penetration. Moreover, the as-SPS processed alloy had an initial porosity of ~30%, which could have caused local heterogeneity within the nitrided region as open and near-surface pores increase the effective area exposed to the nitriding atmosphere and may provide additional pathways for nitrogen ingress. This may lead to local changes in thickness, shape and diffusion depth across the treated cross-section (Lavrys et al., 2023; Zhang et al., 2023a).

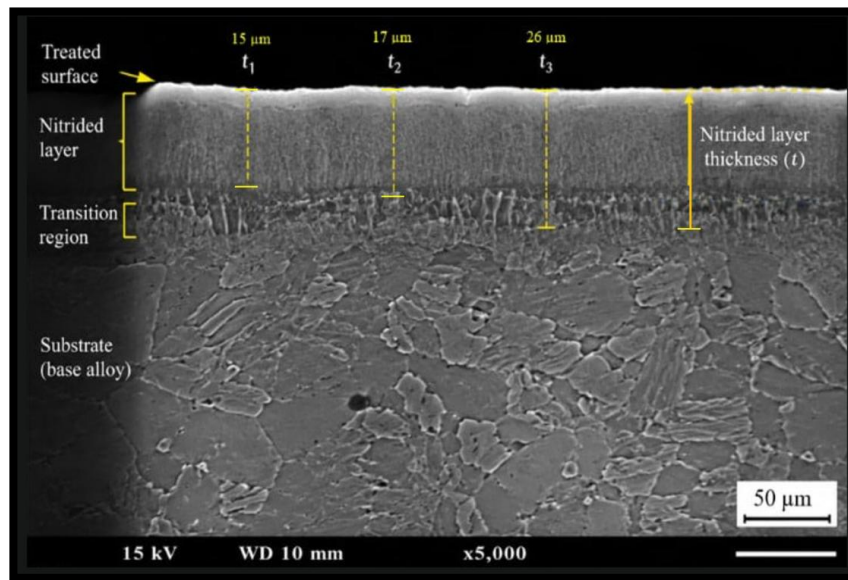


Figure 6. Cross-sectional SEM micrograph of the gas-nitrided Ti-Al-Zr alloy showing the treated surface, nitrided layer, transition region, and underlying substrate.

4. CONCLUSION

In this study, the effect of gas nitriding parameters on surface performance of Spark Plasma Sintered Ti-2Al-2.5Zr alloy was explored using Taguchi design, Gray Relational Analysis and ANOVA. Gas nitriding technique improved surface hardness and significantly lowered wear and corrosion rates compared to untreated SPS alloy. The nitriding temperature was shown to be the most dominant processing parameter affecting the overall performance. The treatment period and nitrogen gas flow rate among the processing parameters tested showed significantly lesser effects. Multi-response optimization indicated that the optimum setting for nitriding was 1050 °C, 35 min and the highest tested nitrogen gas flow condition. The confirmation experiment showed a good concordance between expected and experimental results. XRD and microstructural studies further revealed the formation of TiN and Ti₂N phases and the formation of a relatively thick and continuous nitrided surface layer.

The results show that the combination of SPS and optimized gas nitriding is an effective method to improve the mechanical, tribological and electrochemical surface features of Ti-2Al-2.5Zr alloy. However, biological reactions such as cytotoxicity, cell adhesion, cell proliferation, bioactivity, protein adsorption, antibacterial activity, and apatite production were not evaluated in the current study. Therefore, the data cannot be regarded as adequate to establish the alloy as a therapeutically appropriate material for orthopedic implants. Therefore, the optimized nitrided Ti-2Al-2.5Zr alloy is a good contender for future biological applications. Further investigations including full biological assessment in vitro followed by adequate in vivo evaluation are necessary to evaluate its biocompatibility and long-term biomedical performance.

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Author Contributions

Ekhlas K. Zamel: Experimental investigation, data collection, data analysis, methodology, and preparation of the original manuscript draft. Haydar Al-Ethari: Supervision, methodology, interpretation of the results, review, and editing of the manuscript. Ali H. Haleem:

Supervision, validation, interpretation of the experimental results, and critical review and revision of the manuscript. All authors reviewed and approved the final version of the manuscript.

Ethical issues

Not applicable. This study does not involve any experiments on humans or animals. Hence, ethical approval was not required.

Informed consent

Not applicable.

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Conflict of Interest

The authors declare that they have no conflicts of interest, competing financial interests or personal relationships that could have influenced the work reported in this paper

Data and materials availability

The data generated and analyzed during the current study are available from the corresponding author upon reasonable request.

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