Predicting Surface Hardness of Commercially Pure Titanium Under Plasma Nitrocarburizing Based on Experimental Data

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Abstract. One of the techniques to improve the surface hardness of commercially pure titanium is by using plasma nitrocarburizing. This paper presents an equation to predict the surface hardness with the variable of the treatment temperature and process time of plasma nitrocarburizing. Experimental studies were first conducted to collect surface hardness at different elevated temperatures with different process time. The prediction equation was then developed by using Lagrange’s Multivariable Interpolation method. It is found that commercially pure titanium surface hardness can be predicted as a function of time and temperature. This equation is able to predict the surface hardness of the experimental data with high accuracy. The errors of the predicted hardness to the experimental results are less than 1 percent.

1. Introduction

Titanium has outstanding properties in term of high strength to weight ratio, high corrosion resistance and excellent biocompatibility [1-5]. Nowadays, titanium is widely used in medical and industry field [6-9]. Titanium is widely used in medical field because of its excellent biocompatibility and high corrosion resistance. Its applications involve surgical implement and implants, such as hip ball and socket in hip joint replacement. Titanium application is also in other several medical fields such as bone fitting, dental implant materials, the retaining structure of the heart valves and replacement of the skull [10-12].

Although the hardness properties are considered as outstanding, however when the applications involve sliding conditions, the surface has poor tribological properties. Therefore, when titanium is used as a part of which will experience friction with other parts, for example in hip joint replacement application, the improvement of the hardness value of the surface will be required [13].

The problem occurs when the hardness is increased by a certain treatment to the whole part, there is a possibility the material will become brittle, which is not expected. Any excessive loading applied to the material will damage it easily. Increasing the hardness at the surface without changing the ductility

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properties of materials on the inside of the material will increase the toughness properties of material without changing the ductility in the inner part. This process is referred to as surface hardening.

One of the surface hardening processes is nitrocarburizing. Nitrocarburizing is basically a thermochemical process in which a process of diffusion of nitrogen and carbon atoms toward the surface of metallic materials at certain elevated temperatures. Heat is required to enhance the diffusion of hardening species into the material’s surface. Nitrocarburizing can be applied to liquid, solid, and plasma atmospheres. This is widely used to increase the hardness value in the surface of steel [14, 15].

The plasma nitrocarburizing produces faster nitrogen and carbon diffusion, more friendly with environment, more economical, and, lower gas consumption compared to other nitrocarburizing techniques [16]. The surface hardness improvement as a result of plasma nitrocarburizing process is significantly influenced by the heating temperature and treatment process time. In order to reduce the time and cost in investigating the proper treatment setting of heat and process time to get the expected surface hardness, it is necessary to have an empirical prediction formula for determining the surface hardness as a function of the heat temperature and the treatment process time.

This current research searches the mathematical formula of the surface hardness as a function of heat and time for nitrocarburizing based on experimental results. In this research, the commercially pure (cp) titanium is used. The surface hardness improvement by plasma nitrocarburizing is conducted in various settings of heat and time then the surface hardness is measured. The prediction formula is developed by using Lagrange multivariate interpolation. The formula is derived by considering all experimental data obtained from the plasma nitrocarburizing experiments.

2. Materials and Methodology

The chemical composition of cp titanium is as follows: N: 0.04%, C: 0.05%, H: 0.003%, Fe: 0.13%, O: 0.11%, Al: 0.49% S: 0.03, Ti: balance. Before the nitrocarburizing surface treatment, the hardness value of the material is 53.99 HV.

In the preparation in plasma nitrocarburizing, cp titanium material is cut with the size of 1 cm × 1 cm × 0.3 cm for each specimen. There are six specimens prepared for this purpose. Three specimens are used in the process of plasma nitrocarburizing at 350°C and three specimens are used at 450°C. The surfaces of the specimens are then grinded and polished using polycrystalline diamond until they are all clean and shiny.

In plasma nitrocarburizing process, the plasma is formed in a vacuum by means of high voltage electrical energy in which the positive ions of nitrogen, carbon and hydrogen are accelerated to strike the cathode. The work piece is maintained at a negative DC (direct current) high voltage source of 250-850 volts in the presence of an electric field.

The gases are separated, ionized, and accelerated toward the work piece (cathode). The kinetic energy of ion is converted into heat energy by ion bombardment. This energy not only heats the work piece but also implants ions directly and produces the cathode sputtering. The electrons are forced out from the surface of the work piece. Some of the ions implanted into the surface of the specimen, the other led to the cathode sputtering. Furthermore, absorption and diffusion of nitrogen and carbon atoms led to the formation of the compound layer.

After the plasma nitrocarburizing processes are completed, each specimen is tested of its hardness using micro Vickers hardness tester. This hardness test follows the standard ASTME384. Many researchers have implemented Lagrange interpolation in their works and also published [17-19].

Basically Lagrange give a set of \( k + 1 \) data points, \((x_0,y_0), \ldots, (x_j,y_j), \ldots, (x_k,y_k)\), where no two variables \(x_i\) are the same, the interpolation polynomial in the Lagrange formula is a linear combination.

\[
L(x) = \sum_{j=0}^{k} y_j l_j(x)
\]  

(1)

of Lagrange basis polynomials
Results and Discussion

The results of hardness test showed that the hardness value increased as high as 24.4% when the process time is extended from 120 minutes to 300 minutes. The hardness can be improved as high as 24.4%. The hardness improvement, however, does not show a linear relationship with the process time extension.

For all \( j \neq i, l_f(x) \) includes the term \((x - x_i)\) in the numerator, so the whole product will be zero at \( x = x_i \):

\[
l_f(x_i) = \prod_{\substack{m \neq j \, \forall \ n \neq j \, \forall \ k \neq j \, n}} \frac{x_i - x_m}{x_j - x_m} = 0
\]

on the other hand,

\[
l_i(x_i) = \prod_{\substack{m \neq j \, \forall \ n \neq j \, \forall \ k \neq j \, n}} \frac{x_i - x_m}{x_i - x_m} = 1
\]

All basis polynomials are zero ax \( x_i \), except \( l_f(x_i) \), for which it holds that \( l_f(x_i) = y_i \), because it lacks the \((x - x_i)\) term. It follows that \( y_i = l_f(x_i) \), so at each point \( x_i \),

\[
L(x_i) = y_i + 0 + 0 + \ldots + 0 = y_i
\]

showing that \( L \) interpolates the function exactly.

Lagrange interpolation can be used to develop a multi-variable formula \[20\]. Let \( f = f(x_1, \ldots, x_m) \) is an \( m \)-variable multinomial function of degree \( n \). Since there are \( \rho = (n^{n-m}) \) terms in \( f \), it is a necessary condition to have \( \rho \) distinct points \((x_{1,i}, \ldots, x_{m,i}, f_i) \in R^{n-1}, 1 \leq i \leq \rho, f_i = f(x_{1,i}, \ldots, x_{m,i}) \), for \( f \) to be uniquely defined. This means,

\[
f(x_1, \ldots, x_m) = \sum_{\substack{e_{1} \ldots e_{m} \in E_{n-m}}} a_{e_{1}, \ldots, e_{m}} x^{e_{1}}
\]

where the \( a_{e_{1}, \ldots, e_{m}} \) is the coefficient in \( f \), \( x = (x_1, \ldots, x_m) \) is the \( m \) independent variables of \( f \), \( e_{1}, \ldots, e_{n-m} \) is an exponent vector with nonnegative integer entries consisting of an ordered partition of an integer between 0 and \( n \) inclusive, \( e_{1} = \sum_{j=1}^{m} e_{j} \) is the usual vector dot product, and \( x^{e_{1}} = \prod_{j=1}^{m} x_{j}^{e_{j}} \).

3. Results and Discussion

The surface hardness of cp titanium resulted from plasma nitrocarburizing process are illustrated in Fig. 1. For specimens of the plasma nitrocarburizing processes at temperatures of 350 °C, there is a significant increasing in hardness value when the process time is extended from 180 minutes to 240 minutes. The hardness can be improved as high as 24.4%. The hardness improvement, however, does not show a linear behaviour when the process time is extended. When the process time is extended to 300 minutes, the hardness value is increased only 2.3%. The hardness improvement is not significant when it is compared with that of process time extension from 180 minutes to 240 minutes.

The similar trend appears for the plasma nitrocarburizing processes at temperatures of 450 °C as well. There is a significant increasing in hardness value when the process time is extended from 120 minutes to 180 minutes as high as 17%. However, after the process time is extended from 180 minutes to 240 minutes, the increasing hardness is only 4%.

Figure 1 also shows that hardness value of specimens that are resulted from the plasma nitrocarburizing process at temperature of 450 °C is higher compared with specimens that are processed at temperature of 350 °C.

The results of hardness test showed that the higher the temperature, the hardness value will be higher, and the longer the process time, the higher the hardness value. This is because the diffusion of carbon and nitrogen atoms depends on the process time and temperature. The higher the time and
temperature, the more diffusion of carbon and nitrogen atoms and the distance is longer as well. Furthermore, the layer compound Ti (N, C) which is formed also thicker so the hardness become higher.

The Lagrange polynomial interpolation is solved by using inverse method implemented in FreeMat. The complete equation of the prediction:

\[ Hp(t, T) = 0.00000001591435t^2T^2 - 0.00000831481481t^2T - 0.00125182291667T^2 \\
+ 0.00066025000000t^2 + 0.00112944444445tT + 1.6307812499982t \\
+ 0.53099999999990T - 342.42062499998030 \]  

(1)

The process time range is from 120 minutes to 300 minutes while the temperature range is from 350 °C to 450 °C. From the equation, the highest surface hardness is 127.11 HV at process time 228 minutes and temperature 450 °C. The smallest surface hardness is 40.29 HV at process time 120 minutes and temperature 350 °C. Figure 2 shows the surface hardness curve of cp titanium as a function of process time and temperature that is resulted from this multivariate interpolation method. It can be shown from Table 1 that the predicted surface hardness has high accuracy (error is less than 1%) if the decimal digits of significant are 9 or more.
Figure 2. The surface hardness of cp titanium that is processed plasma nitrocarburizing at temperatures 350 °C and 450 °C.

Table 1. Error in surface hardness value due to the number of decimal digits

| Process Time (Minutes) | Temperature (°C) | Experiment Results (HV) | 14 Decimal Digits | 10 Decimal Digits | 9 Decimal Digits | 8 Decimal Digits |
|------------------------|------------------|-------------------------|-------------------|------------------|-----------------|----------------|
| 180                    | 350              | 74.16                   | 9.97E-06          | 0.08             | 0.45            | 21.69          |
| 240                    | 350              | 92.25                   | 1.42E-07          | 0.11             | 0.64            | 31.03          |
| 300                    | 350              | 94.41                   | 2.16E-07          | 0.17             | 0.99            | 47.41          |
| 120                    | 450              | 103.7                   | 5.28E-08          | 0.04             | 0.24            | 11.38          |
| 180                    | 450              | 121.31                  | 1.00E-07          | 0.08             | 0.46            | 21.94          |
| 240                    | 450              | 126.17                  | 1.71E-07          | 0.13             | 0.78            | 37.54          |

4. Conclusion
Nitrocarburizing plasma increased the surface hardness of commercially pure titanium. By using the multivariate Lagrange interpolation method, a prediction equation is obtained:

\[ H_p(t, T) = 0.000000001591435t^2T^2 - 0.00000831481481t^2T - 0.00125182291667t^2 \\
- 0.00000648680556t^2 + 0.00112944444445tT + 1.63007812499982T \\
+ 0.000660250000000T^2 + 0.5309999999999T \\
- 342.4206249999998030t \]

This equation is accurate with deviations less than 1%.

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