Title	Peculiarities of the α-Ti and δ(TiN) Layers Formation in Plasma Nitriding of Titanium : Theoretical Estimation of the Critical Temperature for the δ Layer Growth in the Low-Temperature Region(Physics, Processes, Instruments & Measurements)
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Peculiarities of the α-Ti and δ (TiN) Layers Formation in Plasma Nitriding of Titanium †

-Theoretical Estimation of the Critical Temperature for the δ Layer Growth in the Low-Temperature Region-

Kalinur SADYROV*, Yasuo TAKAHASHI and Katsunori INOUE*****

Abstract

In the present paper a simplified physical model of the α-Ti and δ (TiN) layers formation is proposed. The calculations were carried out on the basis of the experimental data of other works. Theoretical analysis has been used to determine the critical temperature for the δ layer growth in the low-temperature region. At this temperature the diffusion coefficients of the α and δ layers are equal, i.e. $D_\alpha = D_\delta$. At the intersection point of the D_α-series and the D_δ-series the critical temperature T_{CR} was estimated as 666 ^0C. The predicted intersection point and the critical temperature in the low-temperature region will be determined by experiment in the next report.

KEY WORDS: (Titanium) (Surface Modification) (Simplified Physical Model) (Theoretical Analysis) (Low-Temperature Region) (Critical Temperature)

1. Introduction

Titanium and its alloys have a high specific mechanical properties, such as modulus/density and strength/density, toughness and corrosion resistance. These materials are widely used in different fields, in particular in the aeronautic, aerospace, machinery, electronics, energy and medical industries. However, titanium and its alloys have poor fretting fatigue resistance and poor tribological properties. To realize the full benefit of these materials in friction and wear applications, surface modification treatments are required to effectively increase near-surface strength with lower friction and minimal wear in sliding. In order to modify the tribological properties of sliding surfaces of titanium components many surface treatments have been used, such as physical vapor deposition[1-3], (including ion implantation, plasma spray and evaporation); thermochemical conversion treatments[4-16], (including plasma nitriding, gaseous nitriding, liquid nitriding, ionic nitriding, laser nitriding, ionic carburising and laser boriding); plating[14]; application of solid lubricants by resin bonding/burnishing[14]; and direct ion beam deposition to produce diamond-like carbon[17]. Among these methods the nitriding by glow discharge is a promising method for modifying the surface properties of materials in order to improve wear resistance and hardness in engineering fields. Ion nitriding is advantageous because the sputtering action generated by the plasma cleans and activates the surface and removes any oxide film which may be present or be formed during processing. This enables the nitriding to be carried out at lower temperatures and with greater reliability of bonding.

According to the Ti-N phase diagram (**Fig. 1**)

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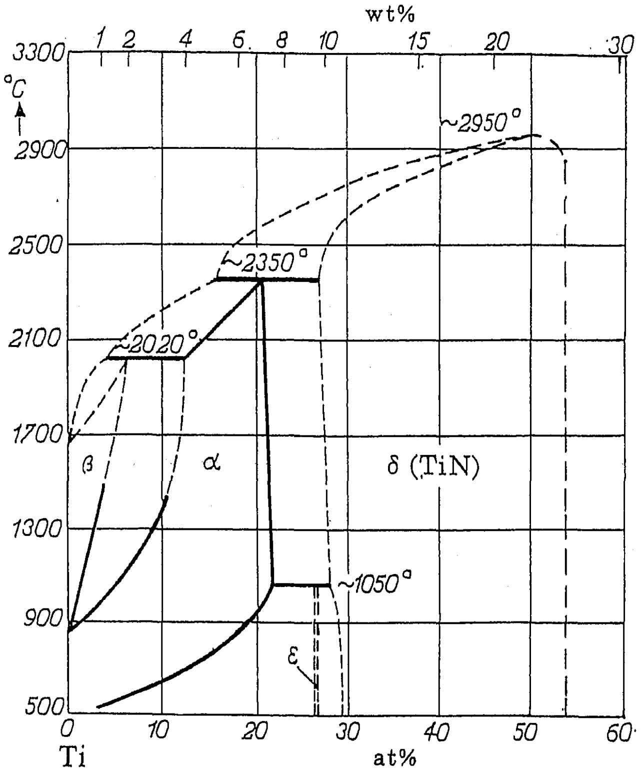

Fig. 1 Titanium-nitrogen phase diagram

from Palty et al[18], during ion nitriding of titanium, depending on the temperature employed, δ (TiN), ε (Ti_2N), α (α-Ti) and transformed β layers are produced. If the treatment temperature is above the β transition (882,5 °C), δ, ε, α and β layers are produced. When treatment temperature is below the β transition, δ, ε and α layers begin to grow. Formation mechanisms for these layers have been extensively described in many studies [4-7, 9,10,12, 19-23] over the temperature range from 700 °C to 1700 °C. Konuma and Matsumoto[6] have carried out studies at T = 800-900 °C, Metin and Enal[9] at T=800-1080 °C, Salehi et al[10] at T=700-950 °C, Bacci et al[21] at T=900-1000 °C, Wasilewski and Kehl[19] at T=900-1570 °C, Eremeev et al[20] at T=1350-1700 °C, Repkin et al[21] at T = 1300-1670 °C, Wood and Paasche[22] at T=800-1080 °C, and Bars et al[23] at 1350 °C and 1450 °C.

Antilla et al[24] have measured the diffusion coefficient of nitrogen in α-Ti by annealing nitrogen-implanted titanium samples in the low-temperature region from 450 °C to 700 °C and the Arrhenius plots were illustrated along with previous results[19-21]. We can see in their plot over the wide temperature region T=450-1670 °C no curving or discontinuity.

Also the Arrhenius analyses for diffusivities in the δ, ε and α phases were carried out by Metin and Enal[9] in the temperature region T=800-1080 °C, and showed that the values of diffusivity in δ, ε and α layers are different and that $D_\varepsilon > D_\alpha > D_\delta$. Theoretically in this case the thickness of the ε layer should be greater then the thickness of the α layer, but many experimental data[4-7, 9, 12, 22,23] show the thickness of the α layer to be greater than the thickness of the ε layer. If we consider the values of D_α and D_δ, theoretically and practically the thickness of the α layer should be greater than the thickness of δ layer in the temperature region above 800 °C. In Figure 12 of Reference 9 with lowering temperature the values of D_α decrease more sharply than the values of D_δ. **Fig. 1** shows with lowering temperature the solubility of nitrogen in α-Ti is decreased, this also has been confirmed by several studies[18, 23-27].

We can suppose that these two curves of D_α and D_δ have a crossing point where $D_\alpha = D_\delta$ at some fixed temperature and the thickness of the α layer will be equal to the thickness of the δ layer. With further lowering of temperature below a crossing point we can expected that $D_\delta > D_\alpha$ and the thickness of the δ layer will exceed the thickness of the α layer because the δ-solubility is greater than that of α. This is important as a technological point, when we need to obtain a δ layer with a small α layer, preserving the core of the materials without modification. The purpose of this paper is to find the critical temperature for the δ layer growth in the low-temperature region by theoretical analysis.

2. A simplified physical model of the α-Ti and δ (TiN) layer formation

In order to carry out the theoretical analyses of the α and δ layers formation in the low-temperature region, a simplified physical model is proposed. With this model, we describe the α and δ layer growth behavior. **Fig. 2** illustrates schematically a simplified physical model of δ, ε, α and δ, α layer formation in the low-temperature region.

For the case of δ, ε and α layer formation (**Fig. 2** (a)) according to Takahashi et al[28] we can write the following equations

$$16D_\delta(\tilde{C}_1 - \tilde{C}_2) = k_\delta \sum_{j=1}^{3} \alpha_{1j} k_j \tag{1}$$

$$16D_\varepsilon(\tilde{C}_3-\tilde{C}_4)=k_\varepsilon\sum_{j=1}^{3}\alpha_{2j}k_j \quad (2)$$

$$16D_\alpha(\tilde{C}_5-\tilde{C}_6)=k_\alpha\sum_{j=1}^{3}\alpha_{3j}k_j \quad (3)$$

where D_δ, D_ε and D_α are the diffusion coefficients for the δ, ε and α layers; k_α, k_ε and k_α are the constant for the δ, ε and α growth; $\tilde{C}_1, \tilde{C}_2, \tilde{C}_3, \tilde{C}_4, \tilde{C}_5$ and $\tilde{C}_6$ are the normalized concentrations.

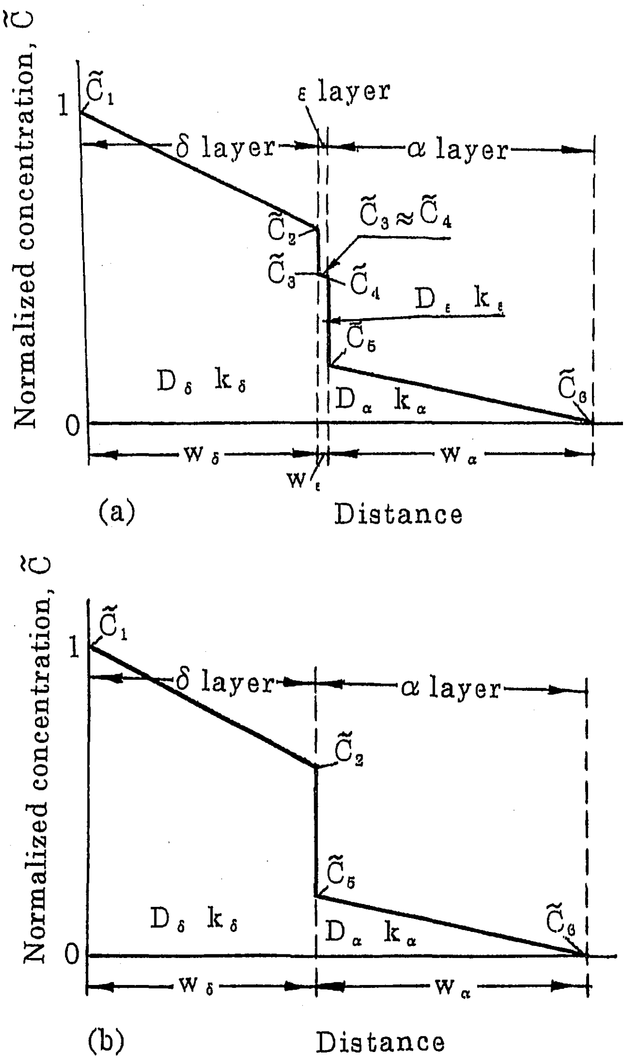

Fig. 2 Schematic illustration of simplified physical model:
(a) formation of the δ, ε and α layers
(b) formation of the δ and α layers

From **Fig. 1** we can see that the ε-phase region is too small and $\tilde{C}_3=\tilde{C}_4$ (**Fig. 2** (a)), therefore ($\tilde{C}_3$ - $\tilde{C}_4$) = 0 and also $k_\varepsilon = 0$.

Hence, Eqs (1) and (3) can be rewritten for the case of δ and α layers formation (**Fig. 2** (b)) in the next form

$$16D_\delta(\tilde{C}_1-\tilde{C}_2)=k_\delta(\alpha_{11}k_\delta+\alpha_{13}k_\alpha) \quad (4)$$

$$16D_\alpha(\tilde{C}_5-\tilde{C}_6)=k_\alpha(\alpha_{31}k_\delta+\alpha_{33}k_\alpha) \quad (5)$$

where $\alpha_{11}=3\tilde{C}_2+\tilde{C}_1$;

$\alpha_{13}=2(2-\tilde{C}_1-\tilde{C}_2)(\tilde{C}_5+\tilde{C}_6)$;

$\alpha_{31}=2(\tilde{C}_5+\tilde{C}_6)(2-\tilde{C}_1-\tilde{C}_2)$; $\alpha_{33}=3\tilde{C}_6+\tilde{C}_5$

From Eqs. (4) and (5) we obtain the diffusion coefficients of the δ and α layers

$$D_\delta=\frac{k_\delta}{16(\tilde{C}_1-\tilde{C}_2)}(\alpha_{11}k_\delta+\alpha_{13}k_\alpha) \quad (6)$$

$$D_\alpha=\frac{k_\alpha}{16(\tilde{C}_5-\tilde{C}_6)}(\alpha_{31}k_\delta+\alpha_{33}k_\alpha) \quad (7)$$

The thicknesses (width) of δ and α layers are in proportion to the square root of time[9, 28]

$$w_\delta=k_\delta\sqrt{t} \quad (8)$$

$$w_\alpha=k_\alpha\sqrt{t} \quad (9)$$

By assuming that the nitrogen concentrations, i.e. the normalized concentrations $\tilde{C}_1, \tilde{C}_2$, $\tilde{C}_5$ and $\tilde{C}_6$ at the given temperature remain constant during processing, from the Eqs. (6)-(9) we can see that the growth of the δ and α layers are dependent on the diffusion coefficients and time. This was also was confirmed by Fast[29] in order to determine a 'penetration depth' or thickness of x layer by using the equation

$$D\cong x^2/2t \quad (10)$$

where D - diffusivity, x - penetration depth and t - time. Therefore, for the following analyses and calculations it is important to take into account the diffusion parameters.

3. The theoretical estimation of the critical temperature for the δ layer growth in the low-temperature region

The diffusivity of nitrogen in titanium is expressed in the general form:

$$D = D_0 \exp(-Q / RT) \quad (11)$$

Where D – the diffusivity (cm²/s), D_0 – the frequency factor (cm²/s), Q – activation energy (kcal/mole), R – the universal gas constant (J/Kmole), T – the absolute temperature (K).

Many investigators[9,19-24] have studied the diffusion of nitrogen in titanium at different temperatures. **Table 1** gives the experimental values of D_0 and Q for α and δ phases. From the analysis of experimental data, the values of D_0 and Q reported by Eremeev et al[20], and Wood and Paasche[22] are considerably different from another works[9,19,21,24]. These deviations have been discussed in previous studies[9,24].

Using experimental data[9,19,21,24] we calculated the diffusion coefficients and have drawn the curves – 1′, 2′, 3′, 4′ for the α layer and – 1, 2, 3 for the δ layer. **Fig. 3** shows the curves of the D_α and D_δ series and their intersection point – B.

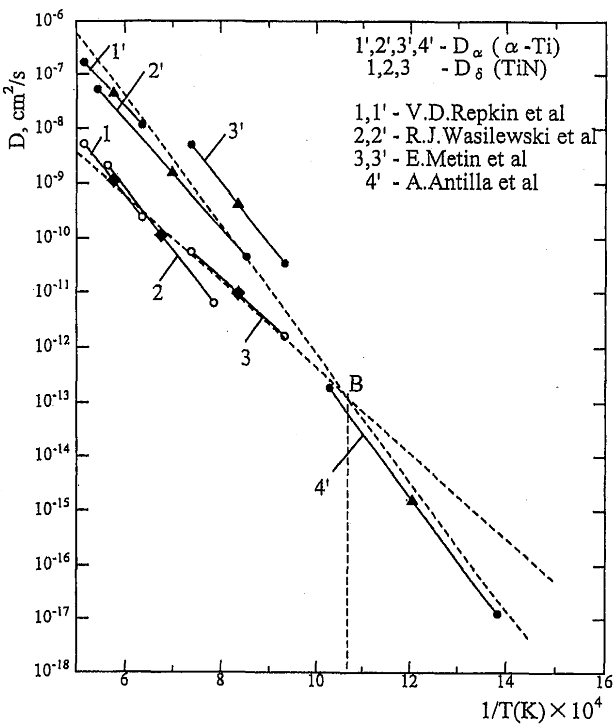

Fig. 3 The curves of the D_α and D_δ series and their crossing point – B

The curves of the D_α and D_δ are described by the following expressions:

for the D_α series

$$LnD_\alpha = -0.746 - 2.716(10^4 / T) \quad (12)$$

for D_δ series

$$LnD_\delta = -10.394 - 1.810(10^4 / T) \quad (13)$$

Solving Eqs. (12) and (13) together, we obtain in the intersection point – B, where the temperature equals 939 K.

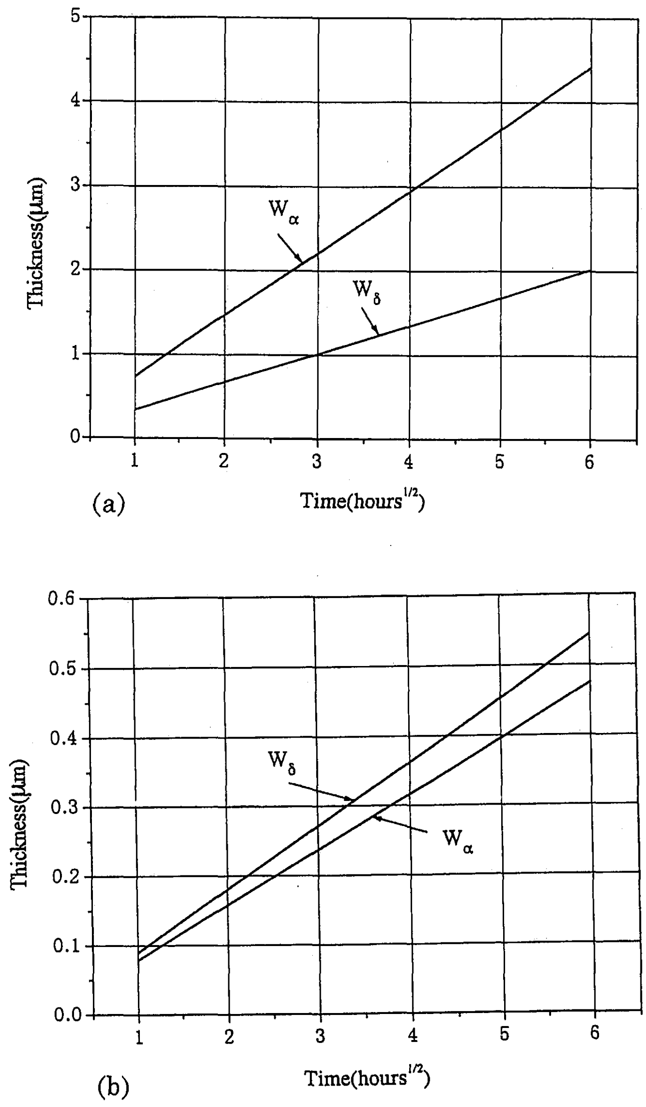

Fig. 4 Growth of the δ and α layers:
(a) at 666 °C;
(b) at 550 °C

This temperature was called the critical temperature T_{CR} = 666 ^{0}C and for both layers the diffusion coefficients $D_\alpha = D_\delta = 1.33 \times 10^{-13}$ cm^2/s applies. At this temperature we can obtain k_δ and k_α as the solution of Eqs. (6) and (7) because we know D_α and D_δ and the values of $\tilde{C}_1, \tilde{C}_2, \tilde{C}_5$ and $\tilde{C}_6$ from the phase diagram (**Fig. 1**): $k_\delta = 5.606 \times 10^{-7}$ (cm/s$^{1/2}$), $k_\alpha = 1.228 \times 10^{-6}$ (cm/s$^{1/2}$). **Fig. 4** (a) shows the growth of δ and α layers at T = 666 ^{0}C. We can see, that the growth rate of $w_\alpha > w_\delta$. Also we can obtain k_δ and k_α at T < 666 ^{0}C, for example at T = 550 ^{0}C. In this case we determine D_α and D_δ from Eqs. (12) and (13) and the values of $\tilde{C}_1, \tilde{C}_2, \tilde{C}_5$ and $\tilde{C}_6$ from the phase diagram as was mentioned above. In the result we obtain $k_\delta = 1.512 \times 10^{-7}$ (cm/s$^{1/2}$) and $k_\alpha = 1.312 \times 10^{-7}$ (cm/s$^{1/2}$). **Fig. 4** (b) shows the growth of δ and α layers at T = 550 ^{0}C. The growth rate of $w_\delta > w_\alpha$. We can suppose that if the nitriding process takes place in the left region from the boundary of diffusion intersection (above 666 ^{0}C) the thickness of the α layer will bigger than the δ layer, and in the right region from boundary (below 666 ^{0}C) the thickness of the α layer will smaller than the δ layer. However, for the predicted theoretical results, the experimental confirmations are required.

4. Conclusion

The nitriding of titanium by glow discharge in the low-temperature region, which is important as one of the methods of surface modification is analyzed by theoretical estimation and by experiment. Based on these results the nitriding processes were carried out at fixed temperatures to obtain the desirable nitride layers.

In this paper, to attain these purpose, a simplified physical model of the α -Ti and δ (TiN) layer formation for theoretical analysis is proposed. The calculations were carried out on the basis of the experimental data from other workers, which have been allowed to determine the critical temperature for the δ layer growth in the low-temperature region. The new definition of the critical temperature is introduced in order to distinguish from the transformation and transition temperatures.

The value of the critical temperature is found to be T_{CR} = 666 ^{0}C. At this temperature the diffusion coefficients of the α and δ layers are equal and also their thicknesses. The predicted intersection point and the critical temperature in the low-temperature region will be determined by experiment in the next report.

Table 1 The experimental values of D_0 and Q in the α and δ phases

Temperature Range, ^{0}C	δ (TiN)		α (α -Ti)		Reference
	D_0,cm^2/s	Q,kcal/mole	D_0,cm^2/s	Q,kcal/mole	
800 to 1080	4.4×10^{-5}	36.5	0.96	51.3	9
900 to 1570	-	-	1.2×10^{-2}	45.2	19
1000 to 1500	5.4×10^{-3}	52.0	-	-	19
1350 to 1700	20	90.0	0.2	57.0	20
1300 to 1670	2.3×10^{-3}	50.2	1.5×10^{-2}	44.0	21
800 to 1500	-	-	8.0×10^{-5}	32.1	22
450 to 700	-	-	0.21	53.6	24

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