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Diffusion kinetics of nitrogen in tantalum during plasma nitriding^①

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[Abstract] The activation energies of nitrogen in tantalum on plasma nitriding conditions were calculated according to the experimental data of hardness of plasma nitriding of tantalum vs time and temperature. The activation energy calculated is 148.873 ± 0.390 kJ/mol. The depth increasing of nitriding layer with time follows square root relation. The nitriding process of tantalum is controlled by diffusion of nitrogen atoms in tantalum solid solution.

[Key words] tantalum; nitrogen; diffusion activation energy

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1 INTRODUCTION

Because tantalum has strong affinity with oxygen it is difficult to nitride tantalum at relatively low temperature (≤ 1000 °C) as compared with its high melting point (2996 °C). Tantalum will be oxidized into Ta₂O₅ rather than nitrided on traditional nitriding conditions of iron and steel^[1]. So nitriding of tantalum reported were done at high temperature and under special condition^[2~7]. Thus there was not enough data about the diffusion of nitrogen in tantalum at low temperature. The diffusion activation energy of nitrogen in tantalum reported were 270.76 ± 48.35 kJ/mol (1700~1950 °C)^[5] and 166.52 kJ/mol (500~1500 °C)^[8], much different from each other. In this paper the diffusion activation energy of nitrogen in tantalum is calculated according to the relation of hardness of nitriding layers of tantalum between time and temperature of nitriding.

2 EXPERIMENTAL

The experiment apparatus was one specially designed for nitriding of tantalum with ultimate vacuum of less than 0.6 Pa, leakage of chamber less than 0.004 Pa/min and highest temperature of 850 °C. The gases incorporated were nitrogen and hydrogen with purity of 99.999%. Tantalum with purity more than 99.6%, $R_z \leq 0.3$ μm and hardness of 110HV_{0.1} was cut into pieces of dimensions 10 mm × 10 mm × 0.25 mm, rinsed ultrasonically in ethyl alcohol. After samples were put in holder made with the same tantalum as the samples in vacuum chamber, vacuumized to 0.6 Pa with incorporated working gases, and heated to given temperature, after definite time cooled to

150 °C then put out. Temperature was measured with both thermocouple and infrared ray methods. And hardness was measured with ZWICK micro-hardometer with load of 1 N. Because the surface nitriding layer was very thin, the apparent hardness measured was the reflection of both practical hardness and thickness of surface layer.

Thickness of nitriding layer of tantalum at low temperature is too small to be accurately measured, while its hardness is very easy to be accurately measured. And it was reported that the thickness of nitriding layer of tantalum is proportional to its hardness^[1]. In fact this conclusion can be deduced according to the volume-mixing law of hardness of surface layer when the depth of stress zone caused by indenter of hardness is much larger than that of surface layer^[9]. If we assume that the relation of depth with time and temperature follows Fick's law and Arrhenius equation respectively, then

$$H = H_0 + K_1 \delta = H_0 + K_1 K_2 \sqrt{D_0 t e^{-\frac{E}{kT}}} \quad (1)$$

which can be rewritten as

$$\ln \frac{(H - H_0)^2}{t} = \ln K - \frac{E}{kT} \quad (2)$$

where H_0 is original hardness of tantalum, $H_0 = 110$ HV; K_1 , K_2 , K , k , D_0 are constants; E is diffusion activation energy; δ is depth of surface layer; t is time and T is temperature.

If the hardness of surface layer obtained at different temperature in different time is regressed according to Eqn. (2) the activation energy E can be gained.

3 RESULTS AND ANALYSIS

3.1 Prior period

The samples of plasma nitriding were in vacuum chamber and in strong electric field, so it was difficult to take any samples out during nitriding. A combined quadratic orthogonal regression experiment plan which contained 15 experiments was employed to investigate the kinetic behavior of nitriding of tantalum when treating time was shorter than 1.5 h. A highly remarkable regression equation of hardness ($H/H_{V0.1}$) vs temperature (T/K) is obtained according to the results of 15 experiments when time was fixed to be 1.5 h, temperature to be 490~710 °C, total pressure 200~600 Pa, original hydrogen mole fraction 0~0.9^[10]:

$$H = 1588.14 - 3.637 T + 0.00228 T^2 \quad (3)$$

If the data of equation is regressed according to Eqn. (2), an E of 148.873 ± 0.390 kJ/mol can be obtained with correlation efficient of 0.9987. The data are shown in Fig. 1(a).

3.2 Whole period

The samples were treated for 1.5 h, 3 h, 4.5 h at temperature of 550, 650, 800 °C respectively and total pressure of 500 Pa, original hydrogen mole fraction of 0.8. There were nine experiments in all. If the data of these experiments is regressed according to Eqn. (2), an E of 158.059 ± 18.371 kJ/mol can be

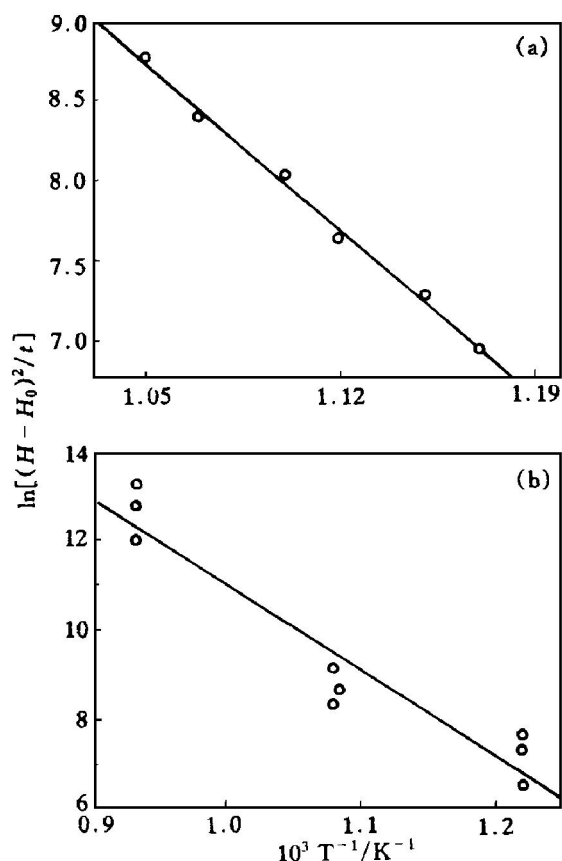


Fig. 1 Experimental data arranged according to $\ln[(H - H_0)^2/t] - 1/T$

obtained with correlation efficient of 0.956. The data are shown in Fig. 1(b).

4 DISCUSSION

It can be seen that both regressions have high correlation efficiencies and similar values of activation energies when treating time is within 0~1.5 h or 0~4.5 h. And the both values of E are near 166.52 kJ/mol reported before^[8]. So it can be thought that all assumptions above are true for the practical circumstances. That is to say, the depth of surface layer is proportional to its hardness. The increasing of depth of nitriding layer of tantalum with time follows square-root relation, which implies that the control step of nitriding of tantalum is diffusion of nitrogen atoms in tantalum solid solution.

Taking the differences of both E into consideration, the diffusion activation energy of nitriding of tantalum on this condition is 148.873 ± 0.390 kJ/mol.

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