LOW TEMPERATURE PLASMA NITRIDING OF PURE TANTALUM FOR INDUSTRIAL APPLICATIONS

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ABSTRACT

Refractory metals such as tungsten, molybdenum and tantalum had been widely utilized as a structural component or part working at the elevated temperature. Among them, the tantalum had significant ductility with low hardness; however, this original nature hindered the working and machining processes. Functional properties related to the tantalum were also attractive to capacitor and high-k dielectric devices; e.g. TaON and TaN thin films by CVD (Chemical Vapor Deposition) processes were expected to be used in industries. In the present paper, a new hardening process of tantalum was proposed: the low temperature high density plasma nitriding. Nitriding experiments were performed at 693 K (or 420 °C) for 14.4 ks. Original pure tantalum had 100 to 120 HV in hardness. This soft tantalum turned to be hardened over 1200 HV after nitriding. Although tantalum nitrides, Ta2N was formed during the nitriding, this significant hardening was driven by the nitrogen solute solid solution into the tantalum matrix.

1. INTRODUCTION

Refractory metals such as tungsten, molybdenum and tantalum have been widely utilized as a structural component or part working at the elevated temperature. The former two refractory metals are brittle and sensitive to a flaw or a notch. On the other hand, tantalum has significant ductility with low hardness; however, this original nature hinders its working and machining processes. Functional properties related to the tantalum are also attractive to capacitor and high-k dielectric devices; e.g. TaON and TaN thin films by CVD (Chemical Vapor Deposition) processes (Ogura, 2007) are expected to be used in industries. Both the pure tantalum and its nitrides or oxi-nitrides are highlighted in the above; there are very few reports on the surface treatment and surface modification. Among them, the surface modification of tantalum by nitrogen ion implantation (Ensiger, 1995; Hatada, 2006) reveals that bcc-structured solid solution is mainly formed by enrichment of nitrogen to tantalum transportation ratio. This solid-solution treated tantalum or Ta (N) has nearly the same nitrogen content as 4 at% in the Ta – N phase diagram (Terao, 1971). Those processes in all were concerned with thin film deposition and modification; there have been little or no reports on the surface modification of bulk tantalum.

The authors (Aizawa, 2013; Santoyoyo, 2014; Aizawa, 2014-1) have been concerned with research and development of the high density plasma nitriding system to describe the hardening process of various metals and alloys and to make nitriding of metallic parts and components. In particular, the martensitic stainless steels were hardened by solid solution at lower temperature under high nitrogen solute concentration (Aizawa, 2014-1; Katoh, 2014; Aizawa, 2015). This formation of bcc-type solid solution in the Fe – N system suggests that other metal and nitrogen systems could be modified to form the bcc-type solid solution without any nitrides via the high density plasma nitriding process.

In the present paper, pure tantalum is plasma-nitrided at 693 K for 14.4 ks to demonstrate that the bcc-type solid solution is formed with or without synthesis of tantalum nitrides. Micro-hardness testing reveals that the pure tantalum is significantly hardened over 1200 HV by this solid solution formation. This significant hardening is driven by the anisotropic crystalline expansion where the octahedral vacancy sites in the bcc-structured tantalum as well as its tetrahedral vacancy sites are occupied by diffusing nitrogen solute atoms. This lattice expansion is analyzed by XRD and EDX.

2. EXPERIMENTAL PROCEDURE

2.1 High Density Plasma Nitriding

High density plasma nitriding system was set-up for solid-solution hardening of metallic parts. Different from the DC- or RF-plasma generators, where the plasmas are ignited and generated in the frequency of 13. 56 MHz or its multiples, the present high density nitriding system has no mechanical matching box with slow response time

of 1 s to 10 s to adjust the applied power. Since input and out powers are automatically matched by frequency adjustment around 2 MHz, the matching response time is only limited to 1 ms at most. This prompt power control provides to make full use of meso-plasma pressure range over 50 Pa. Figure 1 depicts the high density plasma intruding system.

Fig. 1 High density RF-DC plasma nitriding system. ① Vacuum chamber, ②RF-generator, ③Control-panel, ④RF- and DC-power generator, ⑤Evacuation units, and,⑥Carrier gas supply.

Different from the conventional processes, the vacuum chamber is electrically neutral so that RF-power and DC-bias should be controlled independently from each other. A dipole electrode is utilized to generate RF-plasma; DC bias is directly applied to the specimens. Heating unit is located under this DC-biased cathode plate. The emissive light spectroscopy (PMA-11, Hamamatsu, Co. Ltd.) as well as the Langmuir probe system (ALP System, Impedans, Co. Ltd.), are instrumented to the present plasma nitriding system to make quantitative diagnosis on the generated nitrogen plasmas. Through the preliminary studies, the nitriding conditions were optimized as listed in Table 1. In the following experiments, this optimal condition is utilized for plasma nitriding of pure tantalum.

Table 1: The typical plasma nitriding conditions to be employed in the present plasma printing.

Process	Parameters
Pre-sputtering	DC(500V) Nitrogen (70 Pa) at 693 K for 1.8 ks
Nitriding	RF(250V), DC(500V) Nitrogen (100 ml/min) Hydrogen (20 ml/min) 70 Pa at 693 K for 14.4 ks

In particular, the flow rate ratio of nitrogen gas to hydrogen gas plays an important rule. After preliminary study (Aizawa, 2013; Aizawa, 2016), this ratio is kept constant by 5:1 in the following experiment. To be discussed later, increases of this ratio results in enhancement of NH-radical formation in the plasmas.

2.2 Specimens

A pure tantalum bar with the diameter of 60 mm was prepared to fabricate the circular disc specimens with the thickness of 3 mm. Table 2 lists the analyzed metallic impurities besides for the tantalum. Carbon, oxygen, hydrogen and nitrogen contents are less than 0.005 mass %.

Table 2 Impurities in the present pure tantalum specimens.

Elements	Impurity mass%
Fe	< 0.001
W	< 0.0008
Mo	< 0.0006
Ti	< 0.0005
Si	< 0.001
Nb	< 0.005
Ni	< 0.005

2.3 Observation and Measurement

XRF （X-Ray Fluorescence） and XRD (X-Ray Diffraction) analysis was performed to describe the solid solution formation by the plasma nitriding. SEM (Scanning Electron Microscope) and EDX (Energy Dispersive X-Ray spectrometry) were also utilized to measure the nitrided layer thickness and to analyze the nitrogen concentration distribution from the surface to the depth across the nitriding front end. AES (Auger Electron Spectroscopy) was used to describe the element depth profiles for tantalum, nitrogen and other impurities. XPS (X-Ray Photoelectron Spectroscopy) was also used to analyze the chemical shift by nitrogen solid solution into tantalum matrix with comparison to tantalum nitrides.

3. RESULTS AND DISCUSSION

Both XRF and SEM-EDX were employed to make structural analyses and to make nitrogen mapping. Micro-Vickers testing was also used to measure the hardness on the nitrided surface.

3.1 Structural analysis and element mapping

Figure 2 depicts the XRF diagram of the nitrided tantalum specimen at 693 K for 14.4 ks for 2θ raging from $35°$ to $40°$. After (Hatada, 2006), the detected three peaks correspond to Ta_2N, Ta (N) and Ta, respectively. This proves that the nitrogen solid solution is formed together with the synthesis of Ta_2N. No TaN peaks were detected in this XRF measurement. The peak shift of the original tantalum by this solid solution formation is detected in the lower angle of 2θ. This implies that some amount of nitrogen interstitials occupy the vacancy sites

of tantalum crystalline structure and that the original crystalline structure expands by itself during the plasma nitriding.
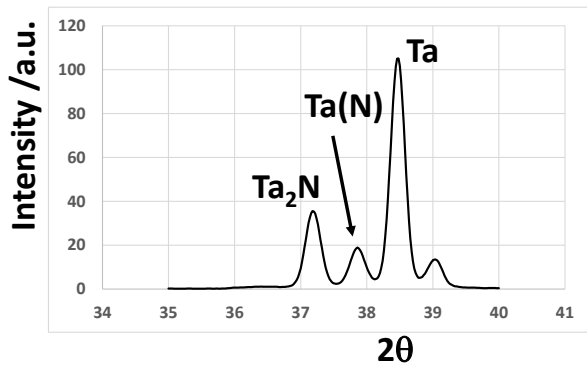

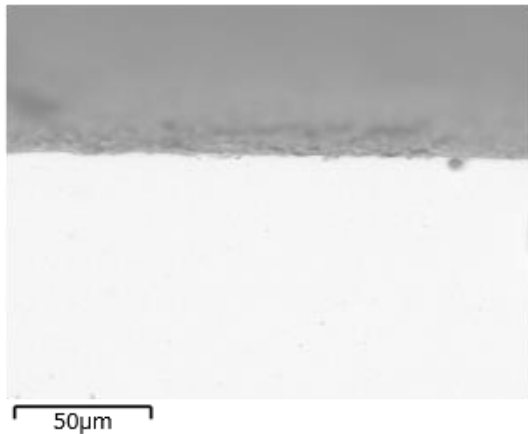Fig. 2: XRF diagram of the plasma nitrided tantalum at 693 K for 14.4 ks.

Fig. 3: SEM image on the cross-section of the nitrided tantalum specimen with the diameter of 60 mm.

The wire-cutting as well as the micro-milling were employed to make a smaller sample for SEM-EDX analysis from the nitrided specimen. Figure 3 shows the cross-sectional image of cut-out specimen with the size of 5 x 15 x 3 mm^3 specimen. The nitrided layer thickness is estimated to be 50 μm.

EDX analysis was performed to make tantalum and nitrogen mappings on the cross-section of nitrided specimen together with the above SEM observation. Figure 4 a) depicts the tantalum mapping; no change was observed even across the nitriding front end at the depth of 50 μm. On the other hand, as seen in Fig. 4 b), the nitrogen contents are much higher in the nitrided layer than those below the nitrided layer. This proves that the nitrided layer in Fig. 3 has high nitrogen concentration than that in the un-nitrided depth of specimen.

In parallel with the nitrogen and tantalum mapping, the oxygen mapping was also made to detect high oxygen contents. As listed in Table 2, there is little oxygen contaminants in the original tantalum; pure nitrogen and

hydrogen gasses were employed in the present plasma nitriding. Hence, high content oxygen distribution into the depth must be related to the nitriding mechanism of tantalum.
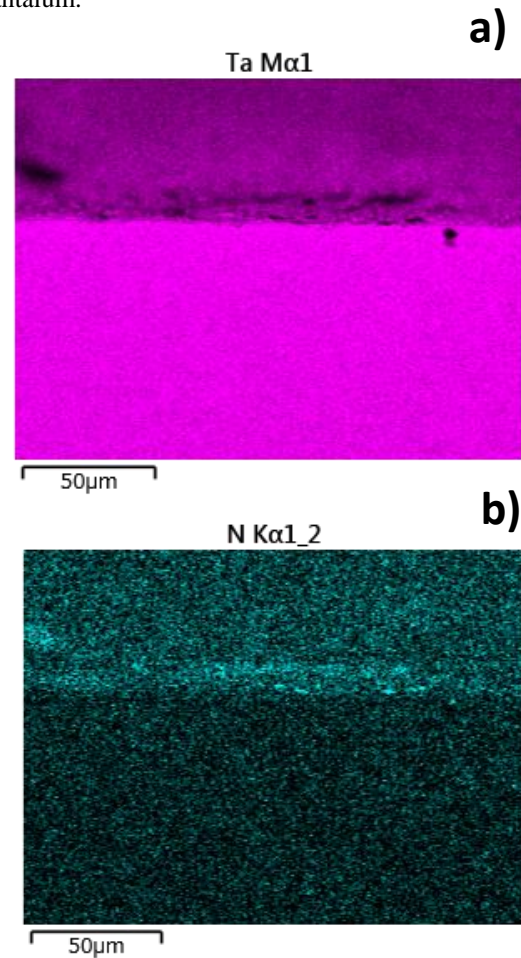

Fig. 4: Element mapping analysis by EDX. a) Tantalum mapping, and, b) Nitrogen mapping.

The average nitrogen content in this nitrided layer reaches to 2 mass% or 7.5 at%. In (Hatada, 2006) and (Terao, 1971), the detected nitrogen content in Ta (N) was limited by 4 at%. This reveals that Ta$_2$N might be synthesized from Ta (N) with extraordinarily high nitrogen solute contents.

3.2 Hardness profile

In the previous works on the nitrogen solid solution (Hatada, 2006), the nitrided layer was too thin to describe the relationship between the hardness and the nitrogen solid solution. The pure tantalum itself has much low hardness; e.g., the measured hardness ranges from 100 HV to 120 HV under the applied load of 0.5 N or 50 gf. Figure 5 shows the hardness profile on the nitrided tantalum surface.

The average hardness measured at ten points on the nitrided tantalum surface is 1270 HV, nearly ten times higher than that before nitriding. Lower hardness measured in the upper part of specimen comes from the shadow effect in the mixed gas flow at the present experimental set-up.

In the above hardness testing, the indentation load was 1 N or 100 gf. This reveals that the nitrided layer thickness is estimated to be 40 to 50 μm in depth; this estimate just corresponds to the nitrided layer thickness measured in Fig. 2.
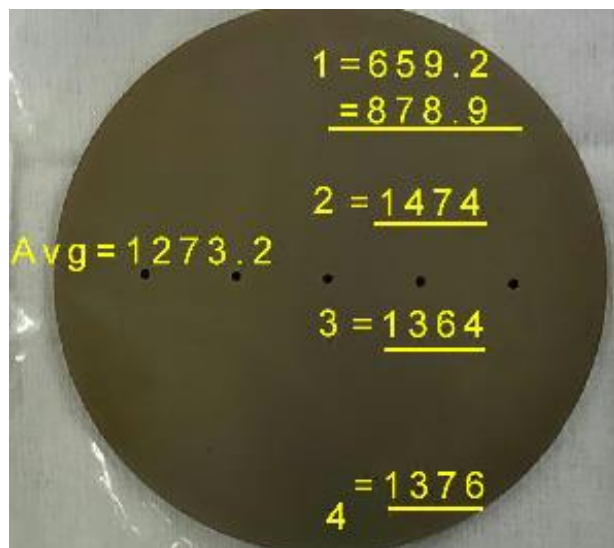

Fig. 5: Hardness distribution on the surface of pure tantalum disc specimen with the diameter of 60 mm.

4. CONCLUSION

High density plasma nitriding process is proposed as a promising surface modification of pure tantalum to significantly harden it by the solid solution strengthening mechanism at lower temperature. In fact, the nitrided tantalum specimen has 1270 HV in average after plasma nitriding at 693 K for 14.4 ks. This high hardness is attributed to nitrogen solid solution with the high content of 2 mass% at the vicinity of surface. The nitrided layer thickness of 50 μm is attractive to industrial application to effective surface modification.

Just as seen in the significant hardening of stainless steels and Fe-Cr alloys by low temperature plasma nitriding, the bcc-type crystalline structures could have more nitrogen solutes at their vacancy sites via the interstitial occupation mechanism. The effect of holding temperature on this solid solution process is to be further studied with consideration on the synthesis process from Ta (N) to Ta_2N. In addition, the gas flow rate effect is also to be taken into account for optimization of this plasma nitriding.

The stability of hardness at the elevated temperature is also investigated through the high temperature hardness testing toward the application of nitrided tantalum substrates as a hot stamping die.

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