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THE EFFECT OF PERIODIC CHEMICAL VARIATION ON THE MECHANICAL PROPERTIES OF Ta FOILS

by

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ABSTRACT

It is known from previous work¹ that the residual gases can play a significant role in determining the resultant chemical purity of vacuum deposited films. The ability to alter the chemical composition and structure of a solid on a micro-dimension scale can provide a means to tailor and control the mechanical properties of the material².

Acetylene gas was admitted to the chamber over two orders of magnitude of pressure during Ta deposition. Residual gas analysis was used to verify that a reaction between the Ta film and the gas occurred. Subsequent auger analysis showed that the carbon in the films could be predicted using a simple pressure vs rate equation.

The pulsed gas process (PGP) has been applied to the electron beam gun deposition of Ta. Tensile test specimens a few micro-meters thick have been produced show fracture strengths varying from ~170 MPa to ~860 MPa for pure to highly pulsed runs. The fracture strength loosely follows a Hall-Petch relation relating fracture strength to the time between pulses. Although diffusion of the carbon smoothes out the chemical period, it is thought that the remaining structure accounts for the strength enhancement.

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INTRODUCTION

An atomistic deposition process can be very powerful in tailoring solid properties provided the condensation process can be properly controlled. Using the correct combination of various parameters, a certain amount of control can be introduced during the condensation. Much work has been carried out to show the effect of substrate temperature on the subsequent structure vacuum deposited pure materials. A few comprehensive models have been proposed to predict the structure in materials as a function of temperature³ or gas pressure⁴. While these models do reasonably well at predicting the structure, the structures available may not be desirable. For example, a columnar structure in a plane foil would not be desirable for enhanced strength. To enhance the strength, some mechanism must be built into the material to impede the movement of dislocations. In this case, a lamellar structure would be desirable.

The Hall-Petch⁵ theory, for strength enhancement of materials, can be derived from considering a periodic array of barriers to dislocation movement. The yield strength of the material can be found to be inversely proportional to the barrier spacing. Whether or not the dislocation is impeded or trapped at the barrier influences the power (n) of the spacing parameter (t) as seen in Eq. 1.

$$\sigma_y = \sigma_0 + k/t^n \quad (1)$$

σ_y is the yield stress; σ_0 is the flow stress; k is a constant pertaining to the details of the structure and type of grain boundaries; and t is the mean separation between barriers. The periodic barrier concept has been successfully applied to vacuum deposited aluminum foils strengthened with oxygen². In the case of tantalum, barriers of carbon should produce a similar effect. The carbon can be introduced by the decomposition of acetylene during the deposition⁶.

Experimental

The depositions were carried out in two electron beam gun systems. One system was diffusion pumped with a cryobaffle while the other was a turbo-molecular pumped system. The tantalum used was 99.97% pure. The tantalum was deposited from unlined copper hearth electron beam guns. A residual gas analyzer (RGA) was used on the turbo system to observe the chamber constituents during deposition and pulsing.

A number of experiments were carried out varying both the tantalum deposition rates as well as the acetylene pressure in the chamber. Depositions at both 300 C and at 700-800 C were carried out with the gas to determine if the substrate temperature would significantly alter the result. Specimens were subsequently analyzed by Auger Electron Spectroscopy (AES) to determine the ratio of carbon to tantalum. A log-log plot of the result is shown in Fig. 1. It should be noted that the data shows no significant difference and follows a straight line. In addition it should also be noted that the inset, showing a typical RGA plot, indicates that the principal gas in the chamber is hydrogen and thus the ionization gauge pressure must be corrected in order to determine the actual amount of acetylene available for the reaction. This "working curve" allows, then, a precise amount of carbon to be introduced to the material during the deposition. By pulsing the gas into the chamber, a layered structure should be produced.

A number of free standing tensile foils were produced by depositing the tantalum onto molybdenum sheets through a mask. The frequency of pulsing was varied for each run. The pulse height of gas remained constant and total pulse width was about one second. The molybdenum was subsequently removed by dissolving in a nitric acid solution. There appeared to be no interaction between the tantalum and molybdenum substrate or between the tantalum and nitric acid as examined by the auger analysis. A problem with the stress in the tantalum foils was observed much below 400 C as the tantalum fell apart during removal. Hence the depositions were carried out at substrate temperature ~500 C.

Results and Discussion

The curve in Fig. 1 shows the carbon concentration as a function of rate deposit and gas pressure.

The data obey the simple relation shown in equation 2.

$$I_f = k \Sigma \lambda_i(\theta, t) \frac{R_{gi}}{R_d} \quad (2)$$

The k is a scale factor to account for differences in the measured gas pressure versus the true gas pressure. λ_i is the sticking coefficient as a function of coverage, ($0 \leq \theta \leq 1$), and temperature t. R_{gi} is the rate of gas impingement and R_d is the rate of deposit. Moving up and down the curve a layered deposit should be produced.

The tantalum foils were evaporated at $\sim 3\text{nM/sec}$ and the pulsed spacing varied from $\sim 32\text{nM}$ to $\sim 270\text{nM}$ and a pure foil. The only sample to show any ductility was the pure sample. The other specimens showed brittle fracture.

Figure 2 shows a plot of brittle fracture versus the pulsed spacing (microns) to the minus one half power. It is quite fortuitous that the fracture strength should loosely follow a Hall-Petch relationship. An argument may be made that at the onset of mass dislocation movement, the material fractured instead of yielding. However, the fact remains that $\sim 5\times$ strength enhancement was observed.

The samples were depth profiled to examine the chemical periodicity. In every sample deposited above 400°C , there was no periodicity found, but rather a uniform concentration of carbon. Upon examination of the diffusion constants for carbon⁷, $\sim 27\text{ kCal}$, it is not too surprising that the carbon diffused through the foil. Simple computation from diffusion theory shows that at $\sim 100\text{ sec}$, the carbon would have diffused uniformly at 50nM . However, at $\sim 10\text{ sec}$, the concentration would be $<20\%$ of the initial value.

Clearly, the greater the separation between pulses, the purer the surface layer appears to the condensing Ta atoms. This may be accounted for by considering the fact that the film thickness is growing linearly in time while the diffusion is progressing at a fraction of that rate. Since the total carbon dose was ~ 20 atomic percent during the brief pulse, a relatively pure Ta layer would be present for thickness spacings $>30\text{nM}$ with a deposition rate $\sim 2.5\text{-}3\text{nM/sec}$.

Other gases such as oxygen and nitrogen were tried. The sticking coefficient of nitrogen on room temperature tantalum approached unity⁸, but the activation energy for diffusion was $\sim 37\text{kCal}$ which would theoretically allow the nitrogen to remain relatively fixed in the sample at temperatures $\sim 400^\circ\text{C}$. However, both oxygen and nitrogen also diffused through the foils, again showing no periodicity.

As a final check of the diffusion problem, a sample was made at $\sim 250^\circ\text{C}$ and depth profiled. As can be seen from Fig. 3, the last carbon layer is reasonably well defined, but as the sample is profiled, the chemical resolution is damped and finally lost.

This lack of chemical periodicity, or markers, in the sample was thought to be catastrophic in that there was no evidence for a periodic barrier and therefore no reason for any strength enhancement except for the small changes in the carbon concentration from sample to sample. An argument correlating the pulse spacing to the total carbon content could be postulated, but since the total carbon content is so low this doesn't seem reasonable.

An alternative argument can be reasoned follows. From nucleation studies and structure studies aforementioned, it is known that the structure of the foil would be a fine grained pseudo columnar structure. If there is a layer of impurity atoms placed on the growing layer, then the following tantalum atoms cannot continue to crystallographically grow as they had previously done. In essence, a new substrate has been provided and a brief disrupted layer could be formed. Since the diffusion takes place at a rate slower than the growth rate, a new steady state growth pattern is established, with relatively pure tantalum at the surface and an advancing set of diffusing carbon atoms below the surface. Since the substrate temperature is well below the re-crystallization temperature $\sim 1000\text{ }^{\circ}\text{C}$, the periodic structure should remain locked into the material even though the production mechanism has diffused away. In this manner, we propose to explain the strength enhancement of the tantalum foils.

Conclusions

The tantalum foils can be significantly increased in strength using the PGP with acetylene. The chemical marker, carbon, appears to diffuse through the foil within experimental times at substrate temperatures $\sim 400\text{-}500\text{ }^{\circ}\text{C}$ necessary for stress relief. Although the carbon diffuses, it is thought that the structure is still disrupted with each pulse and that the diffusing carbon remains below the growing surface due to the differing rates. Since the substrate temperature is below re-crystallization, the structure should remain locked into the material. It is this periodic structure which is thought to give the Hall-Petch type strength enhancement.

Figure Captions

Figure 1

The ratio of carbon to tantalum is plotted on an axis of reduced dimensions, Pa/nM, to correct small variations in deposition rate. The open markers represent runs made at ~300 C. The closed markers represent runs made at ~700-800 C. There is no significant difference in the data. The inset shows a typical RGA spectra during an evaporation. Note the predominance of the hydrogen peak.

Figure 2

The fracture strength of the tantalum specimens is plotted against the pulse spacing to the $-1/2$ power. It is fortuitous that the data fall essentially on a straight line giving a Hall-Petch type dependence. The most significant result is the strength enhancement of about five times.

Figure 3

The Auger depth profile of carbon in tantalum is shown. The sample was made at ~250 C to reduce the diffusion rate so that periodicity could be found. It can be seen from this result that at higher temperatures, the carbon diffuses rapidly enough to wash out any chemical period shortly after the pulse introduction.

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