

CARBURIZING AND DIAMOND DEPOSITION ON TITANIUM AND MOLYBDENUM SUBSTRATES WITH PLASMA JET UNDER REDUCED PRESSURE

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The carburizing and diamond deposition on titanium and molybdenum substrates with argon-methane-hydrogen plasma jets at a pressure of 200 Torr were studied. The deposits were considerably different when different substrates were used. Diamond particles having habit planes were clearly observed in deposits on molybdenum, but deposits on titanium consisted of ball-like particles. TiC or Mo₂C was formed on the respective metal at first, after which diamond deposited on the carbide. In Raman spectra, the sharp line due to diamond was observed in deposits on molybdenum, but the line was broad and considerable amounts of amorphous carbon were included in the deposit on titanium. As the emission spectra from the plasma jets were the same in spite of the difference of the substrates, the difference of deposits on both substrates would depend on the substrate characteristics.

1. Introduction

Diamond thin films have been prepared from methane-hydrogen plasma prepared using microwave discharge under low pressure^{1),2)}. In this procedure, methyl radicals were prepared in the plasma by the reaction between methane and hydrogen. Recently, the deposition of diamond on several substrates in the thermal plasmas of argon-methane-hydrogen mixtures has been reported^{3),4)}. However, only the deposition of diamond was detected in these reports.

Plasma jets prepared at 200 Torr have been applied to the nitriding^{5),6)} and carburizing⁷⁾ of metals. In the carburizing of titanium, CH radicals were identified in the argon-methane-hydrogen plasma jet and the carburizing proceeded easily⁷⁾. When 7 vol.% hydrogen was added to the plasma jet, deposits of diamond were discovered⁸⁾. In diamond deposition by the thermal CVD method, it was concluded that substrate materials which could produce stable carbide layers were good for diamond formation, and that carbide formation was followed by diamond deposition^{9),10)}.

In the present paper, the deposition of diamond of titanium and molybdenum in an argon-methane-hydrogen plasma jet under reduced pressure is studied mainly as to the difference in the deposi-

tion procedure of diamond with different substrates by means of surface analyses.

2. Experimental

Specimens for carburizing and diamond deposition, 20×10×1 mm, were cut from titanium or molybdenum sheets and were polished, degreased, and dried in vacuum. Purified argon, methane, and hydrogen (all 99.9% purity) were used as plasma gases.

The apparatus used for the carburizing and diamond deposition was the same as that used in the nitriding of several metals under reduced pressure⁵⁾. The specimen of titanium or molybdenum was maintained on a water-cooled holder in the reactor. After evacuation of the reactor to below 10⁻¹ Torr, a gas mixture of argon-methane-hydrogen in the desired ratios was introduced into the reactor, the plasma jets were prepared at 200 Torr and the substrates were impinged for the period of 5 min–1 h. The total gas flow rate was 11.8 l min⁻¹ and the DC power supplied was 0.8 kW (40 A, 20 V) in every case. After impinging plasma jets had been carried out for the desired time, the products were identified by scanning electron microscopy (SEM) observation, X-ray diffraction, X-ray photoelectron spectroscopy

line was broad in the deposit on titanium, as shown in Figs. 2a and 2b, respectively. Moreover, considerable amounts of amorphous carbon were included in the deposit on titanium.

As the deposits on both substrates were considerably different, the carburizing reaction and diamond deposition on both metals were investigated in terms of the kinetic data. The relationships between the weight gain of the specimen Δw and the carburizing time t in the carburizing of both metals are shown in Fig. 3 in logarithmic plots. In the carburizing of titanium, the gradient of the line is about 1/2 and the kinetics were represented by a parabolic relationship up to 20 min, after which the gradient of the line changed to 1 and the kinetics were represented by a linear relationship. In the carburizing of molybdenum, a similar tendency was observed, but the weight gain was one order of magnitude smaller than that in the case of titanium and the gradient of the line changed from 1/2 to 1 at about 10 min.

In the shorter carburizing time, the diffusion of carbon in the carbide phase would be the rate-

determining step. After the thick carbide layer was formed, the diffusion was suppressed and diamond was deposited on the carbide phase. In this case, the diffusivity of carbon into molybdenum is considerably smaller than that into titanium¹¹. This is supported by the identification of the species on the metal surface by X-ray diffraction after carburizing for the desired time, as given in Table 1. Diamond was identified with molybdenum carbides after carburizing for 20 min on molybdenum, but it was identified after 50 min carburizing on titanium.

In the C1s of the XPS spectra, the peak due to

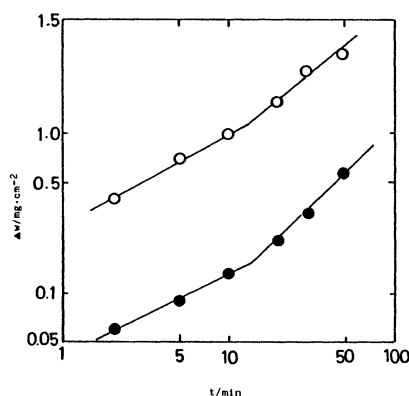


Fig. 3. Relation between weight gain by the carburizing of metals and carburizing time. \circ : titanium, \bullet : molybdenum.

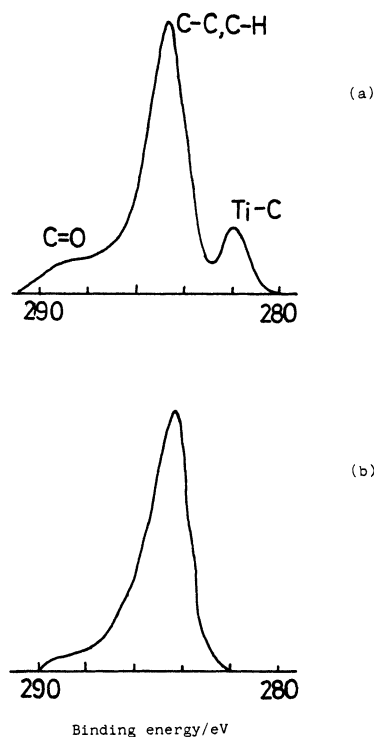


Fig. 4. XPS spectra of C1s on the carburized metals for 20 min. (a) on titanium, (b) on molybdenum.

Table 1. Identified species on titanium and molybdenum carburized with plasma jet by X-ray diffraction

Carburizing time (min)	Identified species	
	on Ti	on Mo
5	TiC, Ti	Mo ₂ C, Mo
10	TiC	Mo ₂ C, γ -MoC, Mo
20	TiC	Mo ₂ C, γ -MoC, Diamond, Mo
50	TiC, Diamond	Mo ₂ C, Diamond, γ -MoC, Mo

the Ti-C bond was identified along with those of C-C and C-H bonds on titanium after being carburized for 20 min, as shown in Fig. 4. The peak almost disappeared after carburizing for 50 min. On molybdenum, the peak due to the Mo-C bond disappeared after carburizing for 20 min, as also shown in Fig. 4, though the peak was identified after carburizing for 10 min. Thus, molybdenum was covered with diamond in a shorter time than titanium.

The relationship between the Vickers hardness of the surface of each metal after carburizing and the carburizing time is shown in Fig. 5. After 10 min of carburizing, the hardness of molybdenum reached 1500 kg mm^{-2} which corresponds to that of Mo_2C . The hardness of titanium reached the hardness of TiC, 2800 kg mm^{-2} , after 20 min of carburizing. After the hardness reached those of the respective carbides, these values rapidly increased and reached about 10000 kg mm^{-2} , which corresponded to that of diamond, in a shorter time.

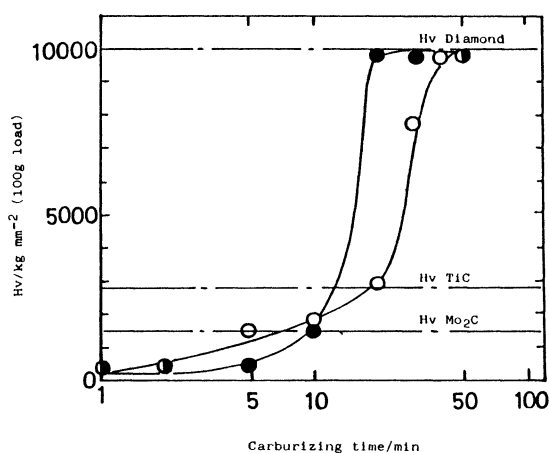


Fig. 5. Relation between Vickers hardness of carburized metals and carburizing time. —○—: titanium, —●—: molybdenum.

From the results mentioned above, diamond was deposited after the formation of respective carbide on each metal. However, both the carburizing and the diamond deposition rates were considerably different on the two substrate materials. As the emission spectra from the plasma jets were the same in spite of the change of the substrate as given in Table 2, the difference of deposit and the deposition procedure of diamond on both substrates would depend on the substrate characteristics. When the plasma jet impinged on the substrate, the surface temperature of titanium was considerably higher than that of molybdenum. At higher temperatures, the carburizing of metals would be increased. Moreover, the diffusivity of carbon in titanium was larger than that in molybdenum. Thus, larger amounts of diamond would deposit on molybdenum than titanium at lower temperatures and the diffusivity of carbon, as diamond is deposited on these metals after the formation of their respective carbides.

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Table 2. Relative intensity of bands and lines observed in plasma jets

Plasma	Relative intensity				
	C ^{a)}	C ₂ ^{b)}	CH ^{c)}	H ^{d)}	Ar ^{e)}
Ar-CH ₄ (0.1%)	15	10	10	12	100
Ar-CH ₄ (0.1%)-H ₂ (2%)	15	5	3	100	30
Ar-CH ₄ (0.1%)-H ₂ (7%)	2	1	1	20	1

^{a)} $2p^2(3s-2p^2(1S))$, ^{b)}Swan system (O-O), ^{c)}4300 Å system (O-O), ^{d)}H β , ^{e)} $4p^3(3P)-4s^3(P)$.

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