NITRIDING AND CARBURIZING OF METALS IN A RADIO FREQUENCY DISCHARGE

Mitsuharu KONUMA, Yasushi KANZAKI and Osamu MATSUMOTO
Department of Chemistry, College of Science and Engineering
Aoyama Gakuin University, Chitosedai, Setagaya-ku, Tokyo 157
Japan

Key words: Nitriding and carburizing metals, Radio frequency discharge
Compounds: TiN, ZrN, TiC, ZrC, NbC, TaC

ABSTRACT

The nitriding of Ti and Zr and the carburizing of Ti, Zr, Nb and Ta were carried out in nitrogen, nitrogen-hydrogen or methane plasmas under 5-20 Torr. The surface of metals nitrided or carburized were hardened by the formation of respective metal nitrides or carbides.

1. INTRODUCTION

The nitriding steel in a glow discharge is called ion nitriding and is carried out in a nitrogen-hydrogen gas mixture at 1-10 Torr pressure (1). Ti and Zr were also nitrided in a same way at 20-40 Torr pressure (2). The authors have studied the nitriding and carburizing of transition metals in nitrogen, nitrogen-hydrogen or methane plasmas prepared by a radio frequency discharge.

In this paper, the nitriding and carburizing procedures are described together with the identification and some properties of the products. The species identified in the plasma and some considerations of the reaction mechanism are also described.

2. EXPERIMENTAL

Materials: Specimens for nitriding or carburizing, 20x10x2 mm^3, were cut from Ti (99.5%), Zr (99%), Nb (99.9%), Ta (99.9%) sheets. The specimens were polished using emery paper and Cr_2O_3 powder degreased in acetone and dried in a vacuum desiccator. Purified nitrogen and hydrogen (99.99999%) were used as plasma gases.
Apparatus and procedures: The apparatus used for the nitriding and carburizing has been described previously (3). Radio frequency power was applied from 500 W crystal controled 13.56 MHz generator made by Japan High Frequency Co. Power was transferred to the gas by means of an impedance matching network. The surface temperature of the specimen placed in the plasma

was determined with an optical pyrometer.

After nitriding or carburizing for the desired time, the weight gain of the specimen was measured by a microbalance. The products were identified by means of X-ray diffraction and ESCA spectrum measurements. The nitrogen and carbon distribution in the products was measured from the intensity of NK_α and CK_α lines. Vickers hardness of the products was determined using a 25 g load. The electrical resistance of the surface layer was measured using four contacts methods.

Mass analysis of plasma gas was carried out with quadrapole mass analyser. The apparatus used for the analysis is shown in Fig. 1. The dc potential of 300-400 V was supplied between a probe anode in the discharge tube and the sampling valve (4). The ions prepared in the rf discharge were extracted through a small orifice in the valve.

3. RESULTS AND DISCUSSION

3.1 Nitriding of Ti and Zr (3, 5, 6)

TiN and ZrN samples are prepared by the direct nitriding of metals in a nitrogen atmosphere under ordinary pressure at high temperatures. The reaction kinetics of nitriding are represented by a parabolic relationship, and the reaction constants are 10^{-13}-10^{-11} $g^2cm^{-4}s^{-1}$ at 800-900°C (7, 8).

The specimens for nitriding were set in the discharge tube and nitrided in desired time under various conditions. As the rf power was supplied, the gas broke down and the specimen was heated. The surface temperature of the specimen increased with increasing rf power and addition of hydrogen as given in Table 1.

The relation between the weight gain w of the specimen of Ti per unit surface area and the reaction time at various powers and nitrogen pressures is shown in Fig. 2 as an example. Similar results were obtained from the nitriding of Ti in nitrogen-hydrogen plasma and the nitriding of Zr in both plasmas. The reaction kinetics are represented by a parabolic relationship, $w^2=kt+c$, as shown by the nitriding of metals at high temperatures. The parabolic rate constant k is given in Table 2. These values were about ten times larger than those obtained when nitriding Ti and Zr in a nitrogen atmosphere at the same temperatures. In both plasmas, k increased considerably with increasing power and increased slightly with increasing pressure. The rate constant in the nitrogen-hydrogen plasma was larger than that in the nitrogen plasma under all conditions.

The color of the surface of the metals changed to golden yellow on nitriding. By means of X-ray diffraction, the product which were formed on Ti by nitriding for longer than 1 h were identified as TiN and Ti_2N. When the nitriding was continued for longer than 8 h only TiN, the lattice parameter of which was 4.26 A was identified. The products which were formed on Zr by nitriding for longer than 1 h were identified as ZrN with small amounts of α-Zr. The lattice parameter of ZrN was found to be 4.59 A.

ESCA spectra of metals and nitrided products are given in Table 3. Strong peaks of Ti2p and Zr3d in the metals and products were identified as based on respective oxides and the weak peaks in the products would be based on respective nitrides. The shift of the binding energy of N 1s in the products is -3 eV and it suggests that the formation of metal-nitrogen bonding.

The intensity of NK_α from a cross section of the products were measured. The intensity decreased gradually with increasing distance from the surface. The curve is similar to the penetration curve obtained for oxidation and nitriding. The nitrogen penetrated 40 μm from the surface. The penetration depth was nearly equal to the sum of the thickness of nitrides and α-solid solutions observed by the microscopic method.

The hardness profiles after nitriding are measured. The hardness gradually decreased with increasing distance from the surface; this decrease was similar to that of the intensity of NK_α line. Addition of hydrogen increased more the depth and hardness. Extrapolation of the hardness curve gave an estimated surface hardness of about 2000 $kgmm^{-2}$ for Ti and 1500 $kgmm^{-2}$ for Zr.

The temperature dependence of the electrical resistance was measured. For the product obtained by nitriding Ti, R_{77}/R_{rt} was 0.17 and $R_{4.2}/R_{rt}$ was 0.07 and was comparable those of Ti. The product was normal down to 4.2 K. The product obtained by nitriding Zr, the superconducting transition was observed. The value of Tc was 10.1 K and it was comparable with that of bulk ZrN (9).

Mass spectrum of positive ions extracted from a nitrogen and nitrogen-hydrogen plasmas are shown in Fig. 3. In the spectrum of nitrogen plasma, nitrogen atomic ion N^+ and molecular ion N_2^+ were identified. In the spectrum of nitrogen-hydrogen plasma, nitrogen-hydrogen molecular ions, NH^+, NH_2^+, NH_3^+ and NH_4^+ were also identified with N^+ and N_2^+. These species would be reactants in the nitriding reaction of metals.

3.2 Carburizing of Ti, Zr, Nb and Ta

Carburizing of Ti, Zr, Nb and Ta in a methane plasma prepared with an rf discharge is described together with the identification and some properties of products.

After the polished metal specimens were placed in a discharge tube, the methane plasma was prepared at a pressure of 10-30 Torr under the rf power of 300-400 W. Carburizing was continued for a period between 30 min and 24 h. After carburizing for the desired time, the products were identified by means of X-ray diffraction method and ESCA spectrum measurement. Some properties of products were measured.

As the rf power was supplied, the gas broke down and the specimen was heated to a surface temperature of 850-900°C. After the discharge, filmy and oily products were observed in the discharge tube. These products were identified as polyethylene and a mixture of higher chain hydrocarbons with the maximum mass number of about 450 by ir absorption and mass spectroscopies, respectively. It is considered that CH_x radicals were produced by the decomposition of methane in the rf discharge.

The color of the metal surface changed to grey on carburizing. Identified phases on the metal surface and lattice parameters of cubic phase after the carburizing were given in Table 4. The lattice parameters are comparable with those for bulk carbides with stoichiometric composition prepared with plasma arcs (10-13).

The binding energies for the products were determined from ESCA spectra. The shift of binding energy of C1s was about -3 eV for TiC and ZrC and about -2eV for NbC and TaC. So the formation of metal-carbon bonding was made sure. Ti2p, Zr3d, Nb3d and Ta4d peaks based on respective oxides were considerably stronger than those based on carbides.

The intensity of CK_{α} line from a cross section of the product decreased gradually with increasing depth from the surface. The apparent diffusion constants of carbon in the metals were determined from the penetration curves using Fick's 2nd law and were $1\text{-}6\times10^{-13}$ cm^2s^{-1}. These values were comparable with those of carbon in the metals at the same temperatures (14).

Superconducting transition temperature Tc was measured with a electrical resistance method. Both of NbC and TaC were superconductors,Tc's of which were 10.2 K and 8.3 K, respectively. These values were slightly lower than those of stoichiometric NbC and TaC prepared with plasma arc (12, 13). Oxides formed on the carburized metals which were found in the ESCA spectra would decrease the Tc.

REFERENCES

(1) M.Hudis, J. Appl. Phys. 44, 1489 (1973).

(2) M.B.Liu, D.M.Gruen, A.R.Krauss, A.H.Reis,Jr., and S.W. Peterson, High Temp. Sci. 10, 53 (1978).

(3) M.Konuma and O.Matsumoto, J. Less-Common Met. 52, 145 (1977).

(4) A.Giraud, "Ion Mass Spectroscopy" in "Reactions Under Plasma Conditions" Vol. I, edited by M.Venugopalan, (Wiley, New York 1971).

(5) M.Konuma and O.Matsumoto, J. Less-Common Met. 55, 97 (1977).

(6) M.Konuma and O.Matsumoto, J. Less-Common Met. 56, 129 (1977).

(7) A.Takamura, Nippon Kinzoku Gakkaishi 24, 565 (1954).

(8) C.G.Desmaison and W.W.Smeltzer, J. Elactrochem. Soc. 122, 359 (1975).

(9) O.Matsumoto and K.Abe, Denki Kagaku 43, 75 (1975).

(10) O.Matsumoto and M.Saito, Denki Kagaku 41, 742 (1973).

(11) O.Matsumoto and T.Miyazaki, High Temp. Sci. 5, 40 (1973).

(12) O.Matsumoto and M.Saito, High Temp. Sci. 6, 135 (1974).

(13) O.Matsumoto and M.Saito, Bull. Chem. Soc. Japan 48, 351 (1975).

(14) D.L.Kohlstedt, W.S.Williams and J.B.Woodhous, J. Appl. Phys. 41, 4476 (1970).

Table 1 Surface temperature of specimen

Plasma gas	Surface temperature (°C)	
	200 W	300 W
N_2	800	850
$90\%N_2+10\%H_2$	900	950

Table 2 Parabolic rate constants of nitriding Ti and Zr

P(Torr)		$k(g^2\ cm^{-4}\ s^{-1})$			
		N_2		$90\%N_2+10\%H_2$	
		200 W	300 W	200 W	300 W
Ti	5	3.0×10^{-11}	1.1×10^{-10}	4.0×10^{-11}	1.5×10^{-10}
	10	9.1×10^{-12}	2.4×10^{-10}	1.1×10^{-10}	6.4×10^{-10}
	20	3.5×10^{-11}	3.0×10^{-10}	4.4×10^{-11}	1.5×10^{-10}
Zr	5	1.8×10^{-12}	8.3×10^{-12}	8.9×10^{-12}	3.3×10^{-11}
	10	5.0×10^{-12}	1.4×10^{-11}	1.2×10^{-11}	4.2×10^{-11}
	20	4.0×10^{-12}	1.0×10^{-11}	1.6×10^{-11}	5.2×10^{-11}

Table 3 Binding energies of nitrided Ti and Zr

		Binding energy (eV)		
		Metal	Nitrided metal	
Ti	$Ti2p_{1/2}$	463.4	463.8	461.3
	$2p_{3/2}$	457.4	458.0	454.6
	N 1s	---	396.1	
Zr	$Zr3d_{3/2}$	183.7	183.5	---
	$3d_{5/2}$	182.5	182.2	179.0
	N 1s	---	395.8	

Table 4 Identified phases and lattice parameter of cubic phase on carburized metals

System	Identified phases	a (Å)
Ti - C	TiC, α-Ti	4.32
Zr - C	ZrC, α-Zr	4.70
Nb - C	NbC, Nb_2C, Nb	4.47
Ta - C	TaC, Ta_2C, Ta	4.46

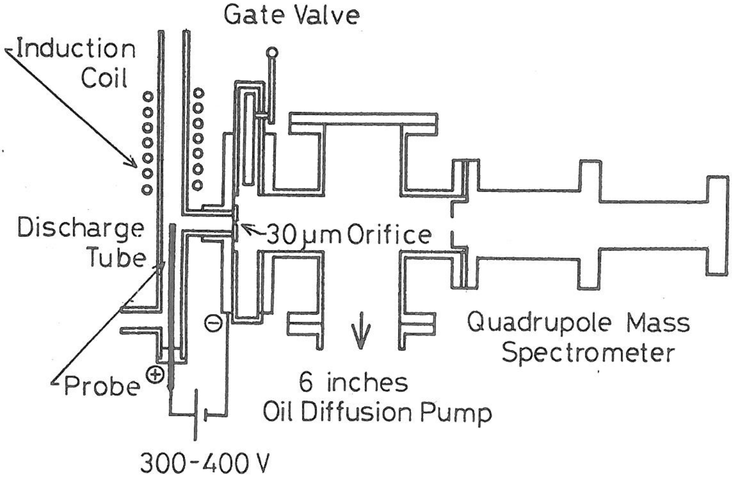

Fig. 1

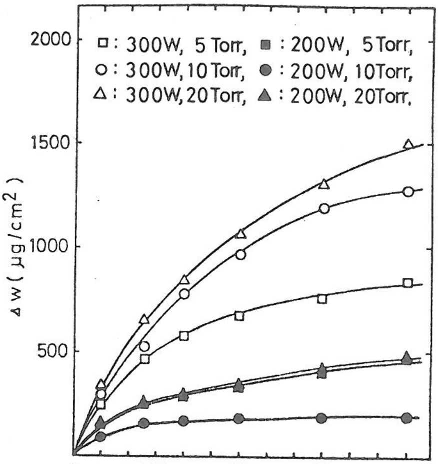

Fig. 2

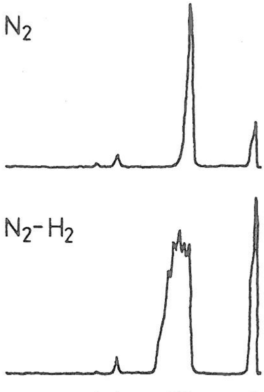

Fig. 3