X-RAY STUDY ON TITANIUM NITRIDE FILMS DEPOSITED BY VCAD METHOD①

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ABSTRACT

TiN films deposited by the VCAD method at the substrate of stainless steel and superhigh speed tool steels are uniform and dense. Their colour, orientation and lattice parameter depend on deposited condition The lattice structure of deposited film, the change of the lattice parameter and its preferred orientation were studied by the XRD method, different behaviours of TiNx film were analysed. The lattice parameter of TiNx films is increased with the nitrogen content and The colour of TiNx film is strongly related to the content of Nitrogen also. The change of preferred orientation depends mainly on the Bias.

Key words: VCAD method, TiN Film, X-ray

1 INTRODUCTION

substrate face properties were improved by depositing TiN with the VCAD method. This technique has being used in industry since ten years ago. There are many reports about the physical, chemical and mechanical properties of deposited TiN films at home and abroad. However there are a few studies concerning about the relationships between the properties and the deposited method and its conditions. There are even very few papers concerning about the colours of depositied TiN film used for decorations. The effects of depositing conditions on crystalline orientation were studied. And the reason of the colour change of decoration TiN film is disscussed in this paper.

2 EXPERIMENT

The vacuum cathodic deposition unit made in China was used for depositing TiNx film and stainless steel O18CrNi9 was used as substrates. Deposition conditions are shown on Table 1.

The structure of deposited layers was analysed by the XRD method. Also the preferred orientation and the lattice parameter of three samples with typical colour were determined. The contents of Ti, C and N were measured by

Table 1 conditions for the deposition of TiNx film by VCAD

Sample No.	1	2	3	4	5	6	7	8	9	0
Bias (V)	−700	−500	−300	−100	0	−700	−500	−300	−100	0
Nitrogen pressure, Pa	1.20	1.20	1.20	1.20	1.20	0.13	0.13	0.13	0.13	0.13

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(XPS). The titanium nitride has a face-centered cubic structure. The geometrical relationship between indices of the crystallographic plane and lattice parameter is shown in equation(1)[1, 2].

$$a=\frac{\lambda}{2\mathrm{Sin}\theta}\sqrt{h^2+k^2+l^2} \qquad (1)$$

where h. k. l– the indices of crystallographic plane; λ–the wave length of $K_{\alpha 1}$ for target Cu; θ–diffraction angle

The preferred orientation degrees were calculated by the interference plane diffraction intensities of preferred specimen to those of random specimens as following formula (2).

$$t=\frac{I(hkl)}{I_0(hkl)} \Big/ \left[\frac{1}{n}\sum_{1}^{n}\frac{I(hrl)}{I_0(hrl)}\right] \qquad (2)$$

where I(hkl) and I_0(hkl) are diffraction intensities of preferred and no preferred orientation respectively; n is the number of diffraction lines; t is the specific value of the preferred orientation.

3 RESULTS AND DISCUSION

X–ray fraction patterns of the samples listed in Table 1 are shown in Fig.1 and Fig.2. The interplanar distance value of diffraction peak of TiN is marked by the number, those without marks are diffraction lines of the substrate of α–Fe and γ–Fe. It is known that deposited layer has only TiN phase. The number of diffraction lines and their shape, intensities of peaks, location of peaks and broaden value of peak are changed with the deppposited conditions. All these phenomenons reflect the changes of the microstructures of deposited film. Results shown in Fig. 1 indicate that the intensities of TiNx (111) diffraction peak increases gradually with the decrease of bias voltage of substrate. The (111) line becomes the greatest when the bias to be 0, it becomes narrowed and sharpened and is accompanied with the weak peaks of (200) and (311). The sum of peaks and its shape are different from the peaks which were loaded by bias. The (220) peak is occurred as the bias is above −500 V and the peak is broader and stronger, when the bias is greater. It demonstrates that there exists microcrystal or the second stress. The position of (111) diffraction line moves to lower angles with the increase of bias at the same pressure of nitrogen and its perfection of crystallization decrease. The preferred orienta- tion of (111) plane is remarkable, and (311) is weak as the bias was at −100 and −300 V res- pectively. The (111) diffraction line is weakend at −500 V and its peak remains only a trace at −700 V. But the (220) diffraction line as well as its peak is increased and broadened obviously at these bias voltages. The TiNx film deposited almost with the crystal plane of (220).

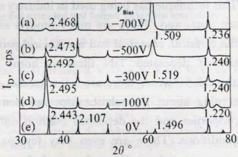

Fig.1 The X–ray diffraction of TiNx film (N_2 pressure: 1.2 Pa)

The colour of film: (a),(c),(e)——red gold; (b)——yellow gold; (d)——grey gold

Fig.2 indicates that there was only diffraction peak of (220) at 0.13 Pa nitrogen pressure and at different bias voltage from −300 V to −700 V. The peak intensities increased and become narrow with the increase of bias which indicates the higher the bias voltage is, the higher the deposition contents are. It is interesting that there is only (111) peak at the bias of −100 V. As shown in Fig.1 and Fig.2, the preferred orientation of these diffraction peaks are slightly increased with the increasing of pressure of nitrogen. Crystallization is better, but no obvious orientation.

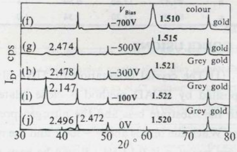

Fig.2 X−ray diffraction of TiNx film under Nitrogen pressure of 1.2 Pa

The relationship between preferred orientation value and bias is shown in Fig.3 which indicates the intensities determination values of various diffraction lines. By the use of Fig.3, it is convenient to find the parameter with specified crystal orientation deposited film of TiNx.

As mentioned above, it is confirmed that crystal orientation of TiNx films deposited by VCAD is influenced by nitrogen pressure and substrate bias voltage. The substrate and cathod were biased by negative voltage, which increased the energy of ion of titanium and nitrogen. The average energy of Ti ions observed by Bergman, Claark[4] was approximately 1.6 e $(10+V_s)$ eV. (V_s−bias) In order to change the V_s, it is essentially to change the energies of posions which arrive at substrate. The posions with different energy may be deposited along the orientation which is benefit to the penetration of posions. Atoms lie on the (111) plane are more than on (220). The density of atoms for each plane was different, and so as their surface energy. Therefore the energy needed for the nucleus forming and growth is different. So the orientation of the deposited film is mainly influenced by bias. The free distance of ions at lower nitrogen pressure is longer and the energy loss is lower. The film of TiNx with crystallographic face (220) would be deposited obviously even the bias is low (−300 V).

The factor which affects the colour should be further discussed . From Fig.1 and 2, we find the interplanar distance of the TiNx film of red colour is shorter than that of gold colour, and that of grey colour is the longest. The lattice parameter of TiNx refinement was made by internal method. The specimen was selected from the samples of different colours. The specimen Si with a size of 15−20 μm and with a purity of 99.999,9% is used as a standard. The results are shown in Fig.3 and Table 2.

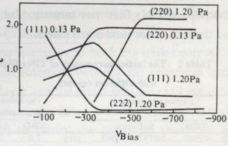

Fig.3 Relationship between preferred orientation value and bias.

Obviously, the value a of TiNx in red is smaller, the value a of gold colour is medium, the value a of grey is the biggest, which indicates that the change of colour may be depended on the lattice parameter. It is well known that the crystal, whether a monocrystal or polycrystal, and its lattice parameter usually change with their composition or the conditions subjected to stress. The TiNx has a face-centered cubic structure. If every position is occupied by titanium and nitrogen atom respectively, it should be Ti:N = 1:1. If the nitrogen pressures and the substrate bias are changed, the proportion of Ti to N is changed and the TiNx will be obtained. When x equals 1, TiN is formed, otherwise TiNx with vacancy either in N or in Ti is formed. It is known that the higher the content of N is, the higher the lattice parameter will be. In this paper, the a value is higher than that of the TiN obtained at standard condition (a = 4.24 Å) The particles which has high energy and velocities, would arrive and deposite on the substrate to form TiNx. The high energy particle bombard force has the similar effect to increase the lattice constant and produces higher a value[6]. But this force does not have an effect on the colour of TiNx deposited by VCAD method. The colour of TiNx film depends on the composition of TiNx. The contents of Ti, N and C of deposited TiNx film were measured by XPS and the results are shown in Table 3.

Table 2 The lattice parameters of TiNx film with different colours.

№	Lattice parameter a Å (25℃) TiNx	Substrate	colour	Thickness of film methods XRD	SEM
h	4.2962	2.8792 ± 0.0003	grey	2.0	2.0
b	4.2654	2.8795 ± 0.0001	red	1.0u	
c	4.2893	2.8791 ± 0.0005	gold	1.4u	

It was confirmed that the sample (b) with higher N content has the higher lattice constant. This result is similar to that of XRD analysis. Therefore, the colour of TiNx film deposited by VCAD depends on the N content and the tiny C.

Table 3 Composition of deposited TiNx film (wt.-%)

№	Ti	N	C	TiN
b	59.02	33.24	2.39	0.5
h	89.47	17.40	0.59	1.4
c	84.19	21.20	1.34	1.0

4 CONCLUSIONS

(1) The crystal orientation of TiNx film deposited by VCAD method is close related with the substrate bias and the nitrogen pressure. When the bias is above −300V and the nitrogen pressure is 0.13 Pa, it will be easy to obtain TiNx film with crystal plane (220), which may be available at the conditions of high nitrogen pressure (1.20 Pa) and high bias (−500V). If the bias is low (< −300V) only the TiNx film with crystal plane (111) is available.

(2) The colour of TiNx film is related to its composition. When the content of nitrogen is increased the lattice constant is tended to increase. When the N% is lower, the colour is red, if it is higher, the colour turns grey, when Ti:N = 1:1 its colour is gold.

REFERENCE

1 Hsu, Shunsheng. Trans. X-ray for Metal. Shangsha

2 Mueller, M. N., *et al.* Trans. MS-ALME, 1958, 212: 39

3 Bergman, C.. In: 15th International Conference on Metallurgical Coatings, San Diego, CA (USA), 11-15 April, 1988