

# Some Properties of TiC Film Deposited on SUS 316L by Ion Plating Method

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## ABSTRACT

Evaluation was made on properties of TiC film, which was coated on the surface of SUS 316L stainless steel by ion plating(IP). As the result, it was found that the thickness of film can be given as linear function of the time of processing and film hardness as linear function of film thickness. In early stage of growth, film shows epitaxial growth along crystal orientation of the SUS 316L substrate. In TiC/SUS 316L interface, orientation of  $(001)_{TiC}/(110)_{TiC}$  was observed. With the increase of the film thickness, there is a trend that growth along a specific orientation of higher degree becomes dominant.

## 1. INTRODUCTION

Because TiC has high melting point and high hardness, it is already used in practical application such as surface reforming of cutting tools, while study is also being made on coating of TiC on Inconel 625 or SUS 316L stainless steel to be used as heat-resistant materials in the applications such as nuclear fusion reactor. For TiC coating on the surface of metal such as stainless steel or high alloy, ion plating method, known as one of PVD methods, is widely used because of extensive applicability, but its properties are not yet elucidated.

Under such circumstances, we coated TiC on the surface on stainless steel by ion plating, and some study was made on the TiC film.

## 2. EXPERIMENTAL PROCEDURE

### 2-1 Specimen and ion plating method

As the substrate for ion plating, SUS 316L stainless steel sheet (No.10 finished) of 2.0 mm in thickness was used, and specimens each in size of 30.0mm(width)  $\times$  130.0mm(length) were cut off from it. Each specimen was fixed on a specimen stand of the ion plating apparatus shown in Fig.1, and TiC vapor deposition (deposition speed :  $0.38\mu\text{m}/\text{min}$ ) was performed in 4 stages : 10 min.(specimen No.1), 15 min.(Specimen No.2), 25 min.(Specimen No.3) and 35 min.(specimen no.4).

### 2-2 Evaluation test

#### 2-2-1 Measurement of TiC film thickness and observation of sectional microstructure.

Cross-section of each of TiC-coated specimens was etched, and film thickness of each specimen was measured using scanning electron microscope(SEM). At the same time, sectional microstructure, near interface of TiC film and substrate were examined metallographically, under SEM and optical microscope.

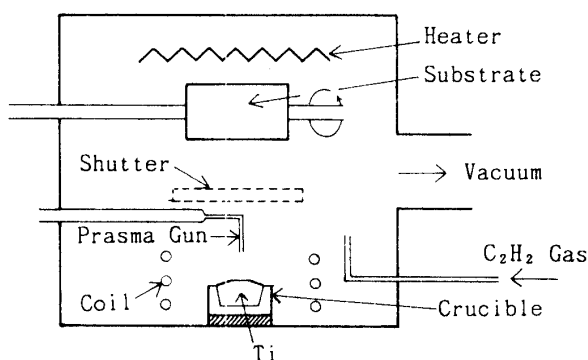


Fig.1 Schematic illustration of ion plating apparatus

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## 2-2-2 Hardness of TiC film (hardness of TiC/substrate composite)

Recently, Burnett and Rickerby et al. reviewed a method to express hardness of film and reported a model<sup>(1)</sup>. This model is primarily to express hardness as a composite of film and substrate, and a mode of expression is based on the rule of mixture. Therefore, the hardness of TiC film discussed in the present study is expressed as hardness of TiC/SUS 316L composite after Burnett et al. because there are already a number of report<sup>(2)</sup> on bulk hardness. Specifically, hardness(HV<sub>s</sub>) was determined by load of 50gr, 100gr, and 200gr using micro Vickers hardness tester on the surface of each of the specimens having different TiC film thickness. Then, the relationship between the measured values and diagonal length of indentation was obtained, and the regularity of relationship between hardness and film thickness was studied.

## 2 2-3 Examination of film surface under optical microscope and SEM

The surface of each specimen coated with TiC was examined under optical microscope and SEM.

## 2 2-4 Observation of transmission electron microscope(TEM) image and electron diffraction pattern near TiC/substrate interface under electron microscope

In order to obtain information on bonding details of TiC film with the substrate, thin film specimen for transmission electron microscope was prepared, and TEM images were observed on the TiC-coated portion, and the portions near TiC/substrate interface and SUS 316L substrate under electron microscope. Then, transmission electron diffraction pattern of each portion was observed, and evaluation was made on crystallographical structure of TiC film and the portion near interface including feature of growth of TiC film on SUS 316L substrate, and orientation relation of crystal plane indices, to study bonding property. Prior to the study, transmission electron diffraction was performed on TiC thin film to confirm that the deposited film was TiC. From the diffraction pattern, study was also made on growing orientation of the film.

## 2 2 5 Texture of TiC film and substrate by X-ray diffraction

Texture of crystal plane to SUS 316L as the substrate of TiC film was studied by the texture obtained using X-ray automatic diffraction apparatus. As the measuring method, Schulz's reflection method was adopted. And the peak of the surface coated with TiC and the surface of SUS 316L substrate, from which TiC film was dissolved by Titanol solution and removed, were searched by wide-angle goniometer, and pole figure was obtained on major planes.

## 3. EXPERIMENTAL RESULTS

## 3-1 TiC film thickness and microstructure

Cross-section of each specimen was examined under optical microscope, and it found that the thickness of TiC film increases with the increase of processing time. As the film thickness increases, defect tended to occur in the film, and it appeared that such phenomenon may be closely related with growing mechanism of TiC film.

In TiC film, film thickness corresponding to each processing time (4.0 $\mu$ m, 5.6 $\mu$ m, 8.8 $\mu$ m and 13.2 $\mu$ m) is obtained, showing good correlation with the processing time. In other words, the thickness of TiC film seems to increase approximately linearly to the processing time within the range of the present study.

## 3-2 Measurement of hardness

Fig.2 shows the results of micro Vickers hardness (HV<sub>c</sub>) as TiC film/SUS 316L composite. From Fig.2, it is evident that the HV<sub>c</sub> of TiC film composite increases as a quadratic curve with the decrease of load, and this value tends to converge to bulk hardness (HV;

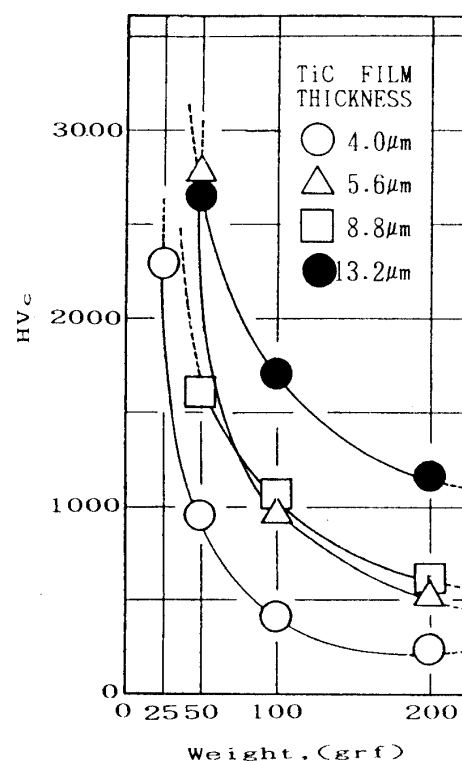


Fig.2 Vickers hardness of TiC film, measured as a composite of TiC film and SUS 316L.

approx.3200<sup>(2)</sup>). On the other hand, according to experimental data of Thomas et al.<sup>(3)</sup> on  $HV_c$ , it was demonstrated that  $HV_c$  can be empirically expressed by the equation (1) with the reciprocal of diagonal length  $D$  of indentation:

$$HV_c = HV_s + (B/D) \quad \text{-----(1)}$$

Here,  $HV_s$  is the hardness of the substrate, and  $B$  is a constant.

Then, in order to find out whether  $HV_c$  of TiC film coated on the surface of SUS 316L can also be expressed by the equation (1) or not, the relationship between surface hardness  $HV_c$  of the specimens Nos.1~4 and  $D^{-1}$  was obtained for each film thickness. As the result, as shown in Fig.3, a distinct linear relation was observed between the hardness of TiC film/substrate composite and  $D^{-1}$ , showing that the relation of the equation (1) exists. If empirical formula

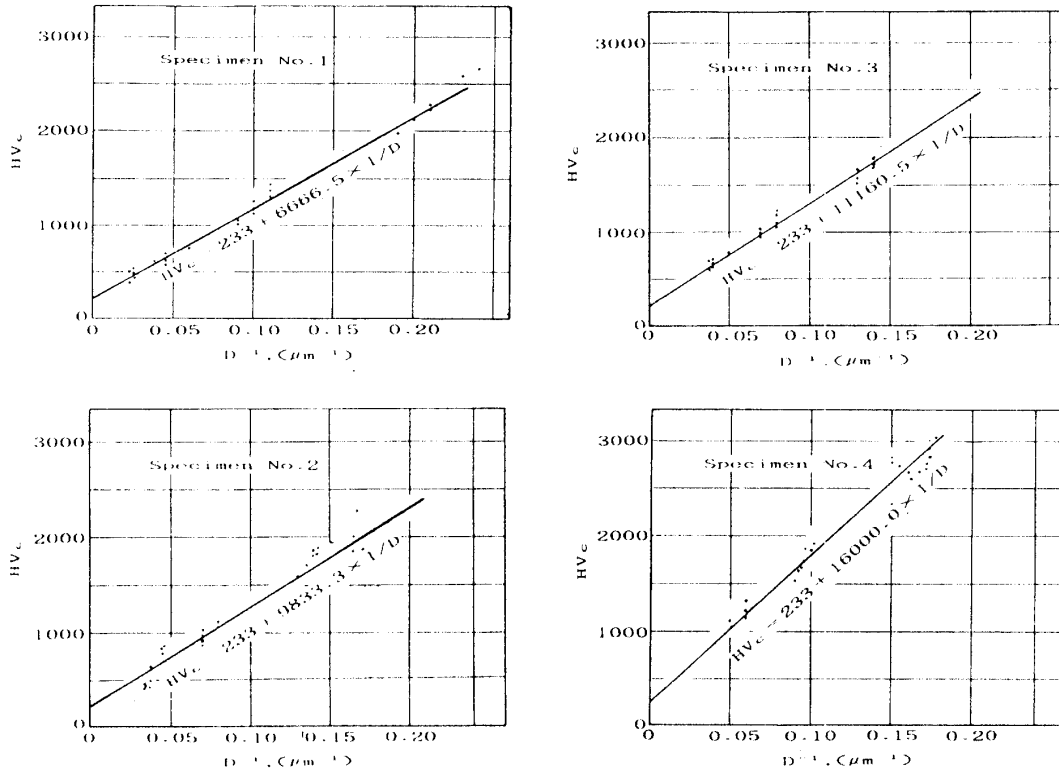


Fig.3 Relation between  $HV_c$  and  $D^{-1}$  of TiC film/substrate composite.

for each film thickness is obtained from the results of Fig.3, it can be given by the equation (2).

$$\left. \begin{array}{l} \text{Specimen No.1 : } HV_c = 233 + 6666.5 \times 1/D \\ \text{Specimen No.2 : } HV_c = 233 + 9833.3 \times 1/D \\ \text{Specimen No.3 : } HV_c = 233 + 11160.5 \times 1/D \\ \text{Specimen No.4 : } HV_c = 233 + 16000.0 \times 1/D \end{array} \right\} \text{-----(2)}$$

On the other hand, approximately linear relation was also found between the thickness and the constant  $B$  as shown in Fig.4 and 5. This suggests that the equation (1) can be expressed as the equation (3), in which film thickness is taken into account.

$$HV_c = HV_s + (Ct)/D \quad \text{-----(3)}$$

Here,  $C$  is a constant, and  $t$  is film thickness of TiC.

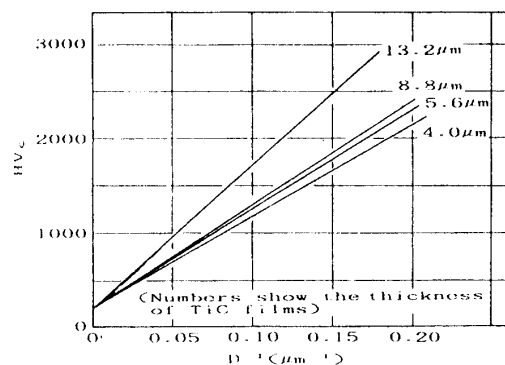


Fig.4 Relation between Vickers hardness :  $HV_c$ , TiC film thickness :  $t$  and reciprocal of diagonal length:  $D^{-1}$

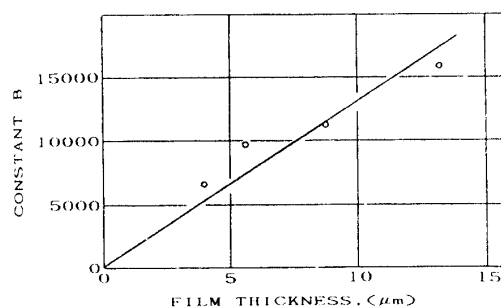


Fig.5 Relation between constant B and TiC film thickness  $t$

The above results reveal that Vickers hardness  $HV_c$  of the TiC film/substrate composite used in the present study can be approximately expressed by the equation (4)

$$HV_c = 233 + (1260t)/D \quad \text{-----(4)}$$

### 3-3 Observation of film surface under optical microscope and SEM

As the result of the examination of the surface of ion-plated TiC film under optical microscope and SEM, the emboss of microstructure of SUS 316L substrate surface was found in the TiC thin film (Specimen No.1 and 2) of 6  $\mu m$  or less, while such embossed structure of substrate was not observed in the specimens No.3 and 4 with thicker TiC film (Fig.6). This mean that the growth of TiC film on substrate surface is achieved by

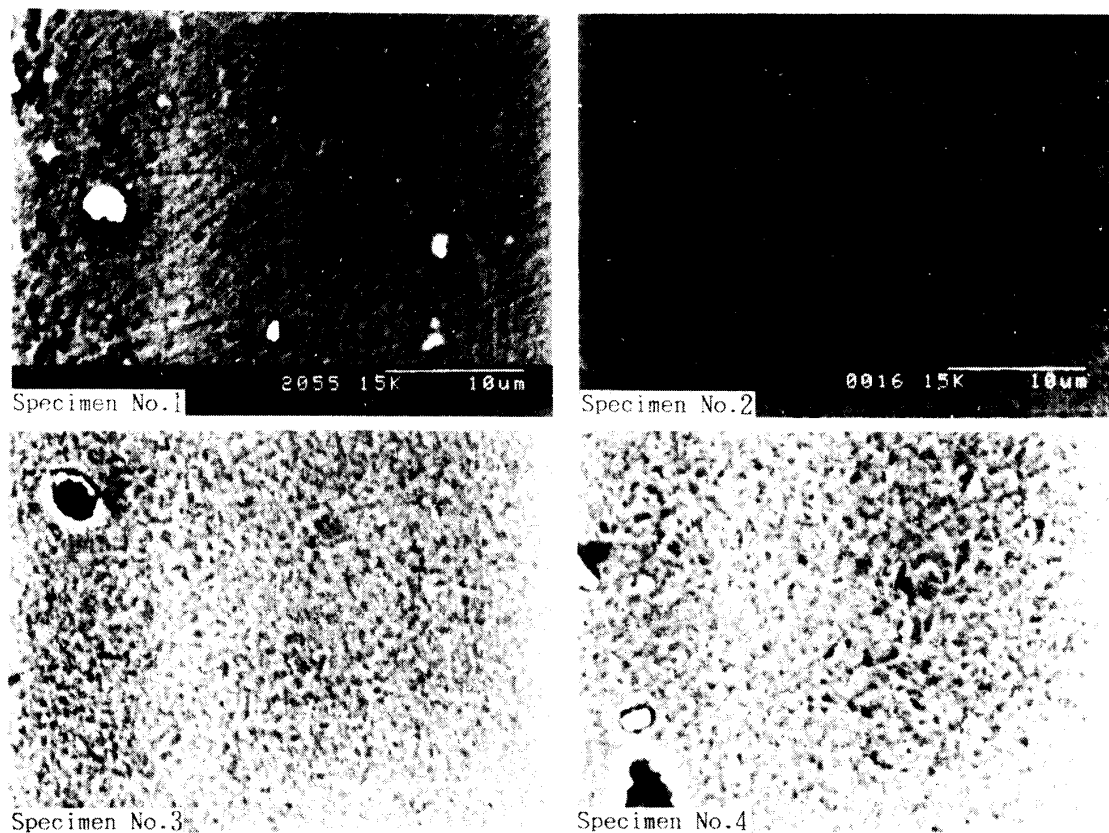


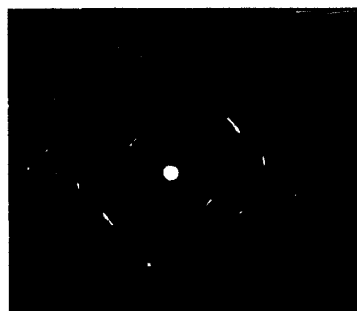
Fig.6 Examples of SEM micrographs observed on the surface of TiC film

epitaxial growth dominated by crystals of the substrate in early stage of growth, but changes occur in the preferred orientation of growth in later stage. However, since it appears that it follows the orientation of substrate crystal in early stage of growth, crystal coordination on TiC/substrate interface seems to be considerably good.

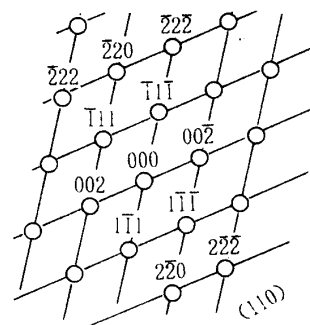
### 3-4 Observation of electron diffraction and TEM images of TiC film and the region near TiC/substrate interface by electron microscope

#### 3-4-1 Results of electron diffraction of TiC film

Fig.7 (a) showse electron diffraction pattern of TiC film stripped from the substrate, and Table 1 represents lattice spacing "d" obtained from Fig.7(a) in comparison with TiC of ASTM X-ray data. From Table 1, it was confirmed that the lattice spacing "d" of the film agrees well with lattice spacing given in ASTM card, and the film was identified as TiC. As indexed in Fig.7 (b), (110) on the surface of TiC film is parallel to the substrate of SUS 316L, and it is recognized that such orientation is dominant in early stage of film growth.



(a) Electron diffraction pattern of TiC film



(b) Plane indices of electron diffraction pattern

Fig.7 Electron diffraction pattern of TiC film stripped from SUS 316L substrate

#### 3-4-2 TEM image and surface orientation near TiC/substrate interface

On the thin film prepared from cross-section of the specimen No.4, electron beam was irradiated in parallel to TiC/substrate interface, and the portion near interface was examined under transmission electron microscope. The results are given in Fig. 8 and 9.

From Fig.8, it is evident that a number of dislocation were noted in SUS 316L substrate or TiC film near interface, and density variations perpendicular to the substrate are found in TiC. This suggest that TiC grows in a direction perpendicular

Table 1 Electron diffraction data of TiC film

$d_{obs}(\text{\AA})$	$I_{obs}$	X-RAY DATA FROM ASTM CARD		
		$d(\text{\AA})$	$I/I_0$	hkl
2.52	M	2.51	80	111
2.11	S	2.179	100	200
1.57	S	1.535	50	220
1.28	S	1.311	30	113
1.12	W	1.255	10	222
1.06	W	1.086	5	400
0.95	W	0.977	5	321
		0.971	30	420
0.87	W	0.884	30	224
		0.833	30	115

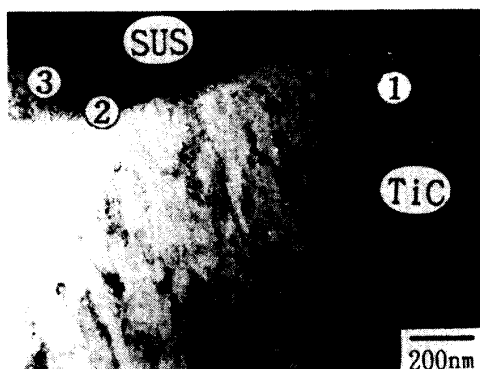


Fig.8 An example of TEM image at a position near TiC/SUS 316L interface

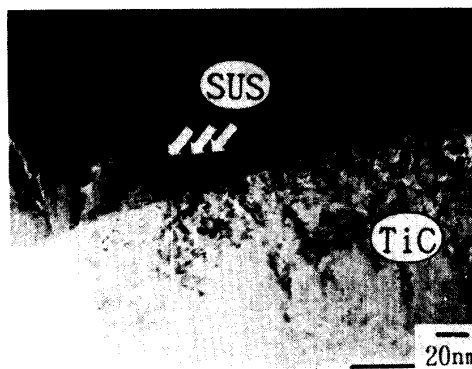


Fig.9 An example of TEM image observed by higher magnification at a position near TiC/SUS 316L interface

to the surface of substrate in needle-like growth, while this must be confirmed by means such as micro beam. Fig.9 reveals the presence of stacking fault with  $\{111\}$  as slip plane or dislocation (arrow) near the surface of SUS 316L substrate. No presence of a third phase on interface is found from these TEM images.

The electron diffraction pattern (a), (b) and (c) of Fig.10 each represents the results of electron diffraction at the following positions respectively.

That is, (a) of Fig.8 : position ① (TiC film); (b) : position ② (TiC film/SUS 316L substrate interface) and (c) position ③ (SUS 316L substrate). Fig.10 (d) shows a sketch of orientation relation of TiC film and SUS 316L substrate transcribed from diffraction pattern.

The above results suggest that  $(110)$  of TiC is parallel to  $(001)$  of SUS 316L, and  $[110]$  of TiC is oriented in parallel to  $[110]$  of SUS 316L substrate. However, these results show orientation relation in limited micro regions, and it is not certain whether these exhibit dominant orientation in wider range or not. However, it is coordinated with lower degree surface of the substrate, and it appears that the bonding of TiC with SUS 316L is very firm. In the present study, diffraction pattern of  $\langle 110 \rangle$  were obtained over almost the entire region of SUS 316L substrate, and this reveals that  $(110)$  of the substrate surface is oriented approximately in parallel to specimen surface.

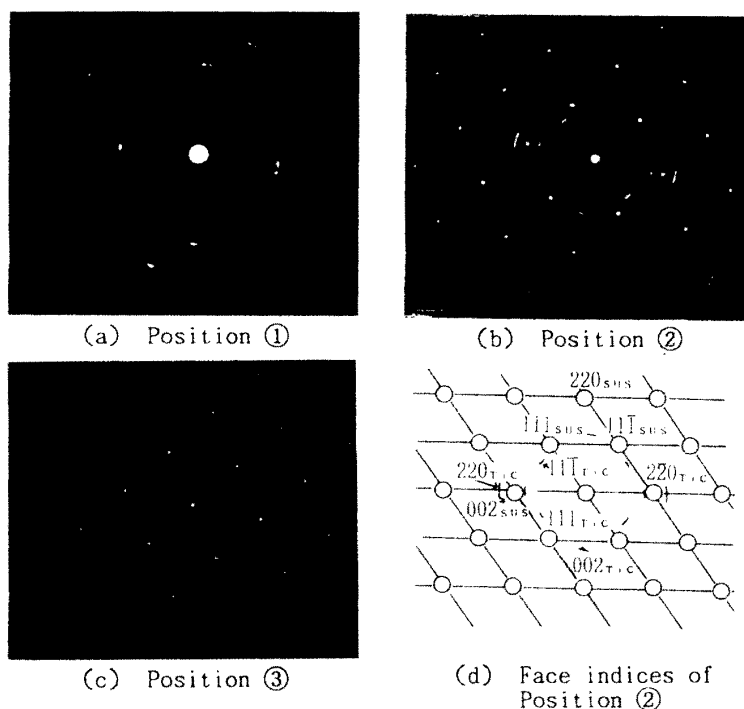


Fig.10 Electron diffraction pattern of Position ①, ② and ③, and face indices of Position ②

### 3-5 Results of observation on texture of TiC film and substrate by X-ray diffraction

Peak search was performed on the surface of TiC film of the specimen No.4 and of SUS 316L substrate (in parallel to rolling direction). As the result, major patterns of TiC, i.e.  $d=2.50479$  (111),  $2.17115$  (200),  $1.53536$  (220), etc. were obtained from TiC film, and major patterns of SUS 316L, i.e.  $d=2.07598$  (111),  $1.80110$  (200),  $1.27228$  (220), etc. were obtained from SUS 316L substrate surface. Thus, pole figure by Schulz's method was obtained on major surfaces of these. The results are given in Fig.11 and 12 respectively.

As it is evident from Fig.12, on the surface of SUS 316L,  $(110)$  shows texture intensively accumulated on sheet surface, and this result approximately agree with the result of electron beam diffraction described above.

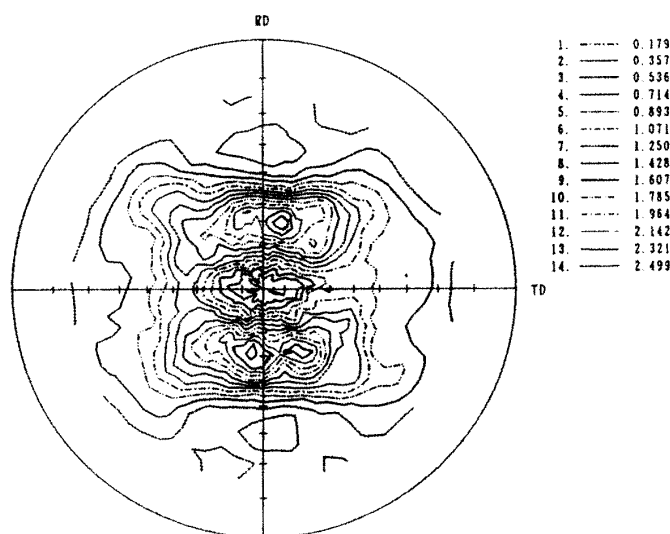


Fig.11 An example of pole figure obtained from (111) on the surface of SUS 316L substrate

With regard to TiC film, all of the diffraction planes obtained by X ray diffraction exhibit texture with normal line getting together near  $\alpha' = 70 \sim 90^\circ$  in pole figure, and this suggests the possibility that accumulation of orientation of higher degree is dominant on the surface of TiC thicker film. This reveals that TiC film grows in early stage of deposition under dominance of the orientation of the substrate, while the preferred orientation is lost when the film reaches a certain thickness and more complicated growth may occur. Thus, it may be necessary to try the calculation of orientation in future for more detailed study of the property of TiC film.

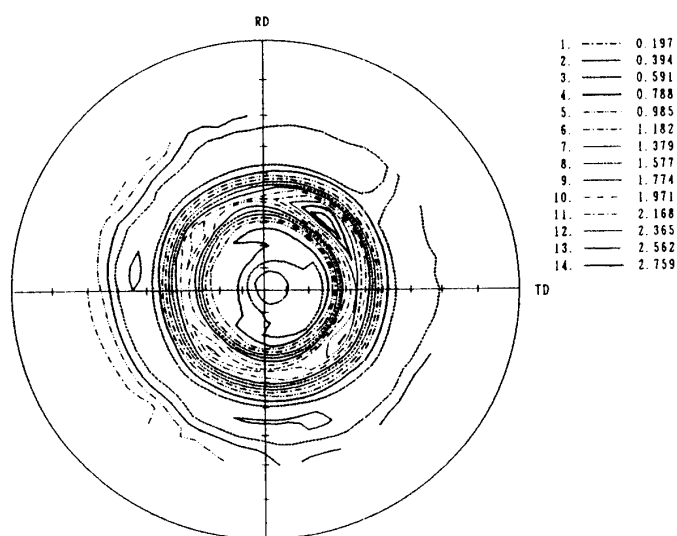


Fig.12 An example of pole figure obtained from (111) on the surface of TiC film

#### 4. SUMMARY AND CONCLUSION

Studies were performed on the specimens, in which TiC film was deposited by ion plating on the surface of SUS 316L stainless steel substrate. The results were summarized as follows:

- (1) The thickness of TiC film corresponds sequentially to the processing time, and film thickness seems to be related linearly to the processing time.
- (2) Micro Vickers hardness  $HV_c$  as TiC film/SUS 316L substrate composite exhibits that the following relation exists between  $HV_c$  and diagonal length of indentation D:

$$HV_c = HV_s + (Ct)/D$$

where  $HV_s$  is hardness of the substrate, C is a constant determined by film thickness, and t is film thickness.

- (3) On the surface of TiC film, crystal structure of the substrate is seen as emboss in case of thinner film of about  $6 \mu\text{m}$  or less in thickness. In early stage of growth of TiC film, epitaxial growth along crystal orientation of the substrate is predicted.
- (4) TEM image near bonded interface of TiC/SUS 316L shows the presence of stacking fault or dislocation with  $\{111\}$  as slip plane near the interface of the substrate, but no presence of a third phase is noted. On the TiC, density variations perpendicular to the surface of substrate are seen and this suggests needle-like growth in a direction perpendicular to the substrate.
- (5) Electron diffraction pattern of TiC film shows that the film is TiC (NaCl type) with (110) coordinated in parallel to the substrate surface. Electron diffraction pattern on TiC/SUS 316L substrate interface shows coordination of  $(001)_{\text{SUS}} // (110)_{\text{TiC}}$ , and this conformity between crystal lattices suggests strong bonding property in the interface. Further, when thicker TiC film specimen without emboss of substrate was examined by Schulz's method, the texture showed pole figure with (110) plane of the substrate intensively accumulated on surface. The surface of TiC film showed the texture with all of major planes getting together near the point where  $\alpha' = 70^\circ$  in the pole figure. This suggests that, in case of a thicker film of  $6 \mu\text{m}$  or more, the growth predominantly occurs along a specific orientation of higher degree.

#### References

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