The Fiber Texture of Thick Anodic Oxide Films on Several Rare Earth Metals in $\text{Na}_2\text{HPO}_4\text{-H}_2\text{O}$ -Ethylene Glycol Solution

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The thick anodic oxide films ($1.5\sim 2.0\ \mu\text{m}$) on polycrystalline rare earth metals such as samarium, gadolinium, dysprosium and yttrium were formed in $\text{Na}_2\text{HPO}_4\text{-60\% H}_2\text{O}$ -ethylene glycol solution at 60°C . The transmission electron micrographs showed that the surface of the thick films were composed of the small particles of polycrystalline oxide (particle size; $50\sim 100\text{\AA}$) and the large grains of single crystal oxide (grain size; $1.0\sim 2.0\ \mu\text{m}$). The crystal structure and the texture of the films were studied by X-ray powder diffraction, X-ray pole figure and electron diffraction methods. Both the particle and grain structures of crystal were found to be body centered cubic, that is, Sm_2O_3 , Gd_2O_3 , Dy_2O_3 and Y_2O_3 (Mn_2O_3 type), respectively. The weak $[111]$ fiber texture whose fiber axis was parallel to the growth direction of anodic oxide film was confirmed in all experiments.

1 Introduction

Recently anodic oxidation of rare earth metals has been of interest for its possible application to the capacitor^{1,2)} and the analysis of anodization mechanism of the metals which are chemically active³⁾. The amorphous anodic oxide films on several rare earth metals such as lanthanum⁴⁾, cerium⁵⁾, samarium⁶⁾, neodymium⁷⁾, gadolinium⁸⁾, dysprosium and yttrium were formed in the phosphate-ethylene glycol solution containing a small amount of water. But when a large amount of water was added to the solution, the films tended to be crystalline oxide. With samarium, gadolinium, dysprosium and yttrium, the thick polycrystalline oxide films exhibited preferred orientation⁸⁾. The crystalline anodic oxide films on some valve metals have been investigated by many authors using the X-ray and electron diffraction methods^{9~11)}. However, no study on the textures of thick anodic oxide films on metals has been reported. The purpose of this study is to investigate the textures of thick anodic oxide films on polycrystalline rare earth metals in order to elucidate the formation mechanisms of the crystalline and amorphous anodic oxide films. The fiber textures in a metal wire or electrodeposited metals have been extensively

studied by an X-ray pole figure method¹²⁾. Metal cations in anodic oxide film migrate to the outer portion of film layer under the electric field during anodization, while metal atoms in electrodeposited metal do not migrate to the direction of the growth. Therefore, the epitaxial growth of the anodic oxide films on the substrate metal seems to be different from the electrodeposition of metals.

In this paper, the texture and oxide structure of anodic oxide films formed on samarium, gadolinium, dysprosium and yttrium in $0.01\text{ M Na}_2\text{HPO}_4\text{-60\% H}_2\text{O}$ -ethylene glycol solution were examined by means of Schulz method¹³⁾ and also by electron diffraction method. It was found that the $[111]$ fiber texture was developed on the polycrystalline rare earth metals and the crystal structure of the oxide film was a body centered cubic (Mn_2O_3 type).

2 Experimental

Polycrystalline rare earth metals (99.9%) used in this study were supplied by Shin-Etu Chemical Industry Co. Ltd (samarium), Leico Industry Inc. (gadolinium, dysprosium) and Nippon Yttrium Co. Ltd. (yttrium). One surface of the rare earth metal disk of a diameter about 30 mm was polished with abrasive paper (cc-1200-cw) and copper and indium electroless platings were carried out to solder a lead wire on it. Then, they were embodied in epoxy resin to serve as an anode. The other

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surfaces of the metal disks polished with abrasive paper (cc-1200-cw) wetted with ethanol before anodization. The constant voltage anodization was carried out in a 0.01 M Na_2HPO_4 -60% H_2O -ethylene glycol solution at 60°C. By using a constant voltage supply (Y.H.P Model 8186 c), the anodic voltage was increased to give the constant current density (about 13 mA/cm^2). When the terminal voltage was reached to 200 V, the anodic current was allowed to decrease for three hours.

Texture of anodic oxide film was measured with Schulz reflection method. An X-ray diffractometer (Rigaku Denki Co. 2035 type) and a texture goniometer attachment (Cat. No. 2454 D 1) were used to obtain partial pole figures and pole density curves of anodic oxide films. The pole densities were measured in the $\phi=0^\circ$ to $\phi=60^\circ$ region. Operating conditions were summarized in Table 1. The direction in the specimen used to show the pole figure was shown in Fig. 1.

Table 1 Operating conditions for X-ray pole figure measurement

X-ray tube : $\text{CuK}\alpha$ (point focus), 35 Kv, 40 mA
Divergency slit : 1°
Receiving slit : 0.6 cm
scallor : 2000 cps
α : $10^\circ/\text{step}$
β : $24^\circ/\text{min}$

Fig. 1 The direction in the specimen used to show the pole figure

The electron microscope used for the present investigation was a JEOL, JEM-100 B operating at about 80 kV. The surface of the specimen was wetted with methyl acetate and a piece of cellulose film was laid on the surface immediately. Then it was dry-stripped using adhesive tape. A small amount of crystalline oxides was

stripped from the oxide film matrix and adhered to cellulose acetate film. The stripped dry replica and adhesive oxides were coated with 10~20 nm of carbon. The orientation and structure of the oxide films were checked by using an electron diffraction method. The morphology of the crystalline oxide surface was examined by the transmission electron morphology.

3 Results and Discussion

3.1 X-ray diffraction analysis

The anodic current decayed rapidly with time for barrier type oxide film growth in 0.01 M Na_2HPO_4 -5% H_2O -ethylene glycol solution at 30°C in the constant voltage anodization of rare earth metals¹⁴. In this case, the anodic oxide film did not seem to grow so much with time. The X-ray diffraction and electron diffraction analyses indicated that these films were weakly crystallized or amorphous. On the contrary, when the electrolysis was carried out at 60°C in 0.01 M Na_2HPO_4 -60% H_2O -ethylene glycol, the anodic current dropped slowly and reached a high steady value. The film partially dis-

Fig. 2 X-ray powder diffraction patterns of the anodic oxide films on several rare earth metals formed at 200 V for 3 hours in 0.01 M Na_2HPO_4 -60% H_2O -E.G. at 60°C

solved and electronic current flowed as it thickened gradually. The X-ray diffraction patterns of these thick films on substrate metal were shown in Fig. 2. Only one weak diffraction peak of the substrate metal such as samarium (333), gadolinium (101) and dysprosium (101) appears. Another peaks from substrate metals were absorbed by thick anodic oxide films on them. The thickness of the anodic oxide film was roughly estimated to be $1.5\sim 2.0\mu\text{m}$ from the absorbance of X-ray ($\text{CuK}\alpha$), assuming the densities of oxide films and the absorbance coefficients for $\text{CuK}\alpha$ radiation¹⁵⁾. On the other hand, many peaks of yttrium metal was observed in the case of yttrium, since anodic oxide film on yttrium does not seem to absorb the X-ray compared with the other rare earth oxides. Under these conditions the film thickness on yttrium may be the same order as in the other rare earth metals.

Only one broad peak of anodic oxide films appeared at 28.7° , 29.1° , 29.6° and 29.9° corresponding to (222) plane of the body centered cubic, that is, Sm_2O_3 , Gd_2O_3 , Dy_2O_3 and Y_2O_3 , respectively. More broad peak appeared at 48.0° for yttrium corresponding to (440) plane of cubic Y_2O_3 . Any peaks except for the five peaks discussed above did not appear. These results suggested that these crystalline oxide film exhibited a preferred orientation and an average particle size can be estimated by using Scherrer Equation (1)¹⁶⁾, when the strain free particles existed,

$$t = 0.9 \lambda / B \cos \theta \quad (1)$$

where, t =average particle size, λ =X-ray wavelength, B =half width of diffraction peaks, θ =Bragg's angle. Using this equation for Sm_2O_3 , Gd_2O_3 , Dy_2O_3 and Y_2O_3 in Fig. 2, the average particle size was roughly estimated to be $60\text{\AA}$.

3.2 X-ray pole figure

The orientation of these oxide film were determined by an X-ray pole figure method. A complete pole figure can be obtained by both a reflection and a transmission methods. Moreover, the diffraction from the anodic oxide film surface and oxide film cross section are required. However, it is impossible to prepare a specimen suitable for the determination of the complete

Fig. 3 Partial (222) pole figure of the anodic oxide film on yttrium formed at 200 V for 3 hours in 0.01 M Na_2HPO_4 -60% H_2O -E.G. at 60°C

Fig. 4 Partial (222) pole figure of the anodic oxide film on gadolinium formed at 200 V for 3 hours in 0.01 M Na_2HPO_4 -60% H_2O -E.G. at 60°C

Fig. 5 Partial (222) pole figure of the anodic oxide film on dysprosium formed at 200 V for 3 hours in 0.01 M Na_2HPO_4 -60% H_2O -E.G. at 60°C

Fig. 6 Partial (222) pole figure of the anodic oxide film on samarium formed at 200 V for 3 hours in 0.01 M Na_2HPO_4 -60% H_2O -E.G. at 60°C

pole figure of anodic oxide films since the film thickness was small. Therefore, partial pole figures ($\phi=0\sim60^\circ$) were obtained in this investigation (Figs. 3~6). The pole figures of the anodic oxide films for gadolinium, dysprosium and yttrium are roughly symmetrical about the (111) pole as shown in Fig. 3~5, and they exhibit a kind of preferred orientation called fiber texture. The direction of anodic current was parallel to the fiber axis. The pole figure of the anodic oxide film for samarium is not

Fig. 7 Partial (222) pole density distribution curves of the anodic oxide films on rare earth metals formed at 200 V for 3 hours in 0.01 M Na_2HPO_4 -60% H_2O -E.G. at 60°C
A : Yttrium, B : Gadolinium, C : Dysprosium

symmetrical around the pole (Fig. 6). This seems to be attributable to the nonuniformity in film thickness which arises from unavoidable cracks and impurity on samarium metal surface.

The partial pole distribution curves for the anodic oxide films were shown in Fig. 7. These pole densities were obtained by integrating the diffraction intensities between the limits $\beta=0^\circ$, $\beta=360^\circ$. The maximum at $\phi=0^\circ$ is due to [111] component of the texture. Since the curves decay gradually from $\phi=0^\circ$ to $\phi=60^\circ$, the weak [111] texture exists on each anodic oxide.

3.3 Electron diffraction analysis and transmission electron micrograph

Figures 8a~10a show typical micrographs on anodic oxide layer after anodization. Several large dark areas in each micrograph seemed to be crystals of anodic oxide on carbon replica which mechanically stripped from the anodic oxide film matrix. The largest one observed in the center of each micrograph was a single crystal whose diffraction pattern was shown in Fig. 8b~10b, respectively. The electron diffraction patterns of all crystals were hexagonal symmetry and showed the same arrangement. These micrographs may provide a pattern for

Fig. 8 Replica electron micrograph of film surface (a) and electron diffraction pattern of the single crystal of oxide (b) after anodizing on yttrium at 200 V for 3 hours in 0.01 M Na_2HPO_4 -60% H_2O -E.G. at 60°C

(a)

(b)

Fig. 9 Replica electron micrograph of film surface (a) and electron diffraction pattern of the single crystal of oxide (b) after anodizing on gadolinium at 200 V for 3 hours in 0.01 M Na_2HPO_4 -60% H_2O -E.G. at 60°C

(a)

(b)

Fig. 10 Replica electron micrograph of film surface (a) and electron diffraction pattern of the single crystal of oxide (b) after anodizing on samarium at 200 V for 3 hours in 0.01 M Na_2HPO_4 -60% H_2O -E.G. at 60°C

body centered cubic for [111] zone axis. The "d" values of these spots were approximately agreement with the corresponding oxide, when they were calibulated by the standard gold film

evaporated on the carben replica.

Most of the electron diffraction patterns of large crystals appeared in Figs 8a~10a showed the hexagonal symmetry for [111] zone axis and a part of them a rectangular symmetry for [110] zone axis. This results suggested that each single crystal had the same direction perpendicular to electrode surface but randomly orientated to the direction parallel to it. That is to say, [111] zone axis was parallel to anodization current and large single crystals of the anodic oxide had also [111] fiber texture and very weak [110] texture.

A large number of small dark spots observed in most parts of the micrographs did not show the original particles of small oxides but corresponded to the pores from the original particles. The pore size was in the range of about 50 Å~100 Å in diameter. This result roughly agrees with the average particle size estimated by X-ray powder diffraction. This fact suggested that these pores corresponded to the small particles of crystalline anodic oxides and these thick film matrixes were composed of these small particles. The diffraction patterns from the areas of small poes can be obtained when the small crystalline oxides inattentively stripped from the anodic oxide film matrix. Several Debye Scherer rings from these areas indicated that these oxides were polycrystal (Mn_2O_3 type), but the texture of the oxide film could not be confirmed because of the weak diffraction densities.

On the basis of these facts, it is assumed that in the initial stage of anodization, formation of small crystalline oxides with preferred orientation parallel to the direction of the growth of film was located in oxide film layer and as the film was thickened, most of them crystallized with the same orientation. In the next stage, local Joule's heat due to the local electronic current might play an important role in the growth of the large single crystals with the same orientation of the small oxides, *i.e.* [111] fiber texture. The lattice spacings of cubic cell decrease in the sequence (111), (110) and (100). This might be associated with the [111] fiber texture, since these phenomena were found in four kinds of rare earth oxides whose crystal structures were body centered cubic (Mn_2O_3

type). The factors affecting the formation of the [111] fiber texture in the early stage and the epitaxial growth relationship between substrate metal and anodic oxide should be investigated in detail.

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会員のページ

オランダにおける

光電気化学研究の一端をみて

1983年10月初めから中旬にかけて、日本学術振興会の援助による国際共同研究の一環としてユトレヒト市応用化学研究所(オランダの国立応用自然科学研究機関TNOに属する)内 Dr. Mackor の部屋に滞在する機会を得た。まとまった仕事をする時間的余裕はなかったため、応化研内部での討論・セミナーと見学、および光電気化学に関連した研究を行なっているユトレヒト大(Prof. Blasse 研)と Twente 工科大(Prof. Feil 研)とをそれぞれ1日訪問して日程を消化した。Shell 社の中研(アムステルダム市)は最近この分野の研究を打ち切ったとの由で、現在オランダ国内で光電気化学に関わっているのはほぼこの3ヶ所に尽きるようである。

Dr. Mackor は EC の Solar Conversion プロジェクト(83年6月まで)内で一応オランダ代表の立場にあり、このため上記の2ヶ所(特に同じ市内にある Blasse 研)とは緊密な連絡をとりつつ仕事を進めている。また Grätzel (スイス), Tributsch (独) 両教授との国際共同研究も行なってきた。Dr. Mackor の今までの関心は主として光触媒による水分解や CO_2 還元にあったようであるが、高効率の変換システムのみを追求する方向はや

や手づまり状態になってきているため、たとえば良い触媒になるかもしれない新しい固体材料や金属錯体の合成とキャラクタリゼーションという、いわば脇道に入りつつある傾向が感じられた。脇道ではあるがかなり興味深く、また彼自身も誇りにしている最近の成果として、金属中の水素含有量を簡単に測定できる電気化学センサーがある。これは Blasse 研の Schoonman 博士が、光電解生成した H_2 ガスを水素化合物として貯蔵できるような光電解セルを考案中に得たアイディアを発展させたもので、実用化をめざした共同開発が進行中である。一、二年先にはこのセンサーが研究室の主テーマになるとのことであった。この例を含め、光電気化学の分野ではまだまだ面白い副産物が見いだされる可能性があることを強く感じた。なお TNO は、いちおう国立の機関ではあるが、実用的に見込みのありそうなプロジェクトを選定して所要経費の半額だけ支給し、残りは研究責任者が外部から調達しなければならない、というかなり厳しいシステムをとっている。

Blasse 研と Feil 研はそれぞれ蛍光体の基礎研究と分子結晶の X 線構造解析を看板にしている研究室で、光電気化学はいわば副業であった。両者とも、実用化よりむしろ解析的な研究を行なっているが、紙数の都合で詳細は割愛させて戴く。(東京大学工学部 渡辺 正)