

Uniform coating of a crystalline TiO₂ film onto steel plates by electrochemical deposition using staged pulse current

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Abstract A crystalline TiO₂ (c-TiO₂) film was electrochemically deposited onto a 10 cm × 20 cm hot-dip-galvanized (HDG) steel plate at 60 °C from an alkaline aqueous solution containing 0.1 M titanium potassium oxalate dehydrate and 1 M hydroxylamine. The electrochemical deposition was carried out by a galvanostatic method. First, a current density of 10 mA cm⁻² was applied for 5 min, which led to the formation of a uniform coating of TiO₂ on a 1 cm × 1 cm small HDG plate. A crystalline layer was observed, however, only in the central area, whereas the upper and the edge areas were amorphous. Both calculations and experiments confirmed that this was due to the difference of the local current densities in the vicinities of different areas. Next, three different currents (5 mA cm⁻² (2 min), 10 mA cm⁻² (2 min) and 20 mA cm⁻² (1 min)) were applied continuously so that the local current density for each part of the substrate achieved appropriate deposition conditions. The film thus obtained was crystalline in all areas and of uniform thickness.

Keywords Crystalline TiO₂ · Electrochemical deposition · Finite element calculation · Hot-dip-galvanized steel · Staged pulse deposition · Uniform coating

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1 Introduction

Protecting car bodies from environmental corrosion is an important issue for the automotive industry. The corrosion protection has to be durable for many years against environmental effects such as water, salt, acid rain and so on, and the paint on the steel car body alone does not satisfy the requirements.

For this purpose a conversion coating, which converts the first layer of the steel into another form, substance or state, is usually applied. There are several ways of producing the conversion coating. The most promising method is the zinc-phosphating process and it is used exclusively in the automobile construction industry today.

Zinc-phosphating, however, has some disadvantages. For example, the steel is covered with Zn₃(PO₄)₂ · 4H₂O, which is not desirable for the environment because of the phosphorus content. The process also produces much sludge containing not only phosphorus but also heavy metals, especially nickel. Moreover the whole process requires numerous steps such as several cleaning stages, an activation stage and generally a post-passivation stage. A large amount of space is needed and in all the stages chemicals are consumed and toxic waste is produced.

It may be interesting to use a metal oxide layer as a corrosion protective film on metal substrates as a substitute for the zinc-phosphate. Metal oxides are very attractive as coating materials because they possess good thermal and electrical properties, and in general they are more resistant than metals to oxidation, corrosion, erosion, and wear. Several recent studies have reported good corrosion resistivity [1–10].

There are several ways to form such metal oxide layers including radio frequency magnetron sputtering, plasma spraying, chemical vapor deposition, and chemical solution

methods. Among these methods, dry processes (the former three) are not appropriate for industrial purposes because these methods are very cost-intensive and difficult to manage.

Amongst the chemical solution approaches, many studies have utilized a sol–gel method, which is one of the most promising technologies to produce amorphous and crystalline metal oxide coatings. This method is especially useful for coating large substrates uniformly by dip coating or spin coating. The sol–gel method, however, usually needs heat treatment at above ~ 300 °C. It may cause tension between the film and the substrate and can lead to coating imperfections.

Electrochemical deposition is a promising technique for the preparation of transparent crystalline TiO_2 thin films on large area substrates [11]. Recently, Ishizaki et al. [12, 13] reported that the preparation of a c- TiO_2 film without heat treatment was successfully achieved by electrochemical deposition. This method has some advantages for automobile manufacturing such as: (1) since the formation of the c- TiO_2 film is carried out in one-step, the process does not need subsequent treatment steps (e.g. heat treatment), (2) the process is less hazardous and is environmentally friendly, (3) the equipment is not expensive and is easy to scale up. These advantages suggest that the electrochemical deposition of a c- TiO_2 film may be able to replace the conventional zinc-phosphating process.

However, the electrochemical deposition of a uniform coating onto large plates or complex shaped materials is often difficult due to a maldistribution of the electric field.

The aim of this study was to prepare c- TiO_2 layers on $10\text{ cm} \times 20\text{ cm}$ hot-dip-galvanized (HDG) steel plates (zinc coated steel commonly used for car bodies) uniformly by electrochemical deposition.

2 Experimental

Titanium potassium oxalate dihydrate (TPOD) and hydroxylamine from Wako chemicals were used as supplied. The HDG steel was supplied from Krupp-Hoesch Co. Ltd. and was cut into $10\text{ cm} \times 20\text{ cm}$ plates. The plates were washed in acetone and methanol twice and soaked in 2 wt.% Ridoline 1559 (Henkel Technologies) aqueous solution at 60 °C for 10 min. After the treatment the surface of the samples was hydrophilic.

Ten litres of electrochemical bath solution was prepared, which consisted of TPOD, hydroxylamine and distilled water. The pH was adjusted with KOH. The sample plate was located centrally between the counter electrodes ($15\text{ cm} \times 30\text{ cm}$ Pt/Ti sheet (99.99% purity)). An electrode was connected to the top of the sample, and the sample was dipped into the electrolyte leaving a

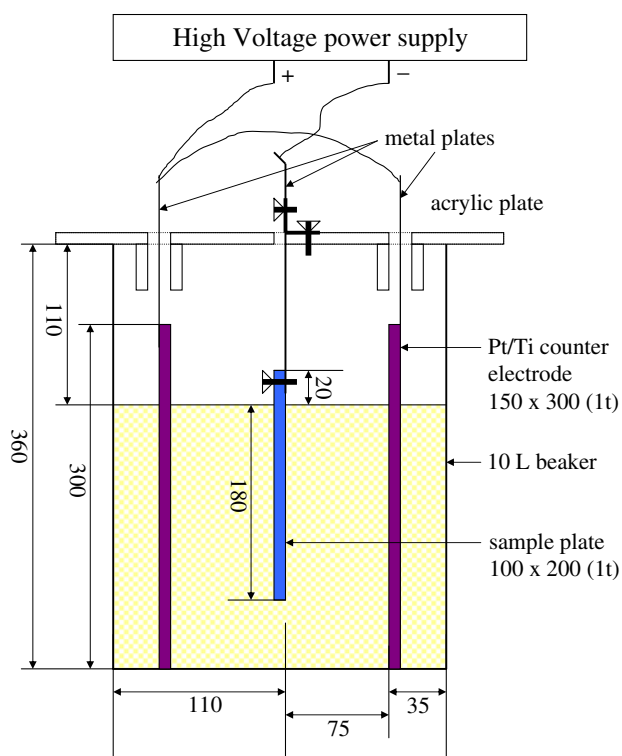


Fig. 1 Schematic figure of whole setup. The numbers in the figure represent the length (mm)

2 cm top edge out of the water. The geometry of the whole setup is described in Fig. 1. The preparation of the TiO_2 film was carried out at 60 °C galvanostatically using a regulated DC power supply (TAKASAGO HX0500-30G).

Prior to the experiments on $10\text{ cm} \times 20\text{ cm}$ plates, the deposition was examined on $1\text{ cm} \times 1\text{ cm}$ samples. For these experiments, the $10\text{ cm} \times 20\text{ cm}$ plates were cut into $1\text{ cm} \times 2\text{ cm}$ small pieces, and a $1\text{ cm} \times 1\text{ cm}$ area was dipped into the electrolyte. These experiments were performed in 300 mL electrolyte with two $3\text{ cm} \times 10\text{ cm}$ counter electrodes. The preparation of the film was done galvanostatically using a potentiostat (Hokuto Denko, HABF501).

The crystal structure of the TiO_2 layer on the substrate was measured by an X-ray diffractometer (XRD) (RIGAKU RINT 2001) using $\text{Cu K}\alpha$ radiation. The morphologies of the surface of the sample plates were observed by a scanning electron microscopy (SEM) (Hitachi SEMEDX-III Type N) equipped with an energy dispersive X-ray fluorescence spectrometer (EDX) (Horiba EMAX EX200). For the $10\text{ cm} \times 20\text{ cm}$ samples, some pieces were cut off from the area 3–4 cm from the top edge (part I), 8–9 cm (part II), 13–14 cm (part III) and 0–1 cm from the bottom edge (part IV), respectively, and used for the observation.

3 Results and discussion

Firstly, coating of a *c*-TiO₂ film was carried out on 1 cm x 1 cm HDG samples using Ishizaki's method. The previously reported condition [12, 13] was as follows: the electrolyte was a 0.05 M TPOD aqueous solution containing 0.5 M hydroxylamine adjusted to pH 9 with KOH, and the deposition was done at 18 mA cm⁻² with stirring. In this study we gradually modified the conditions and finally found the most appropriate conditions to form a *c*-TiO₂ film: The recipe of the electrolyte was 0.1 M TPOD, 1 M hydroxylamine and pH 8 adjusted with KOH. The deposition was done at 10 mA cm⁻² without stirring.

Figure 2 shows the morphology of the TiO₂ layer electrochemically deposited under the conditions described above. The deposition time was 500 s, which is equivalent to a quantity of electricity of 5 C cm⁻². The surface of the sample was completely covered with rod shaped structures with a cross section of ~3 μm. We also confirmed that the morphology was totally homogeneous. The result was perfectly reproducible.

These rods are considered to be crystalline TiO₂ grown by the electrochemical deposition. However, there is still a possibility that the rod shaped structures are not TiO₂ but ZnO crystals grown from the zinc layer on the HDG substrate during deposition. This is plausible because ZnO crystals easily grow toward the *c*-axis and form a rod or a wire. In order to check this point, electrochemical deposition under the same conditions was carried out on cold rolled steel (CRS), which does not have a zinc layer. The result is shown in Fig. 2a. A similar structure appeared on CRS, showing that the rod shaped materials were not ZnO but *c*-TiO₂.

The deposition result was sensitive to small changes in conditions. For example, in the case of the films deposited at 5 and 20 mA cm⁻², only small amounts of crystals were seen, implying that *c*-TiO₂ was formed only in a small range of current density.

Figure 3 shows the XRD spectrum for the (a) HDG substrate before the deposition and (b) TiO₂ film deposited on an HDG sample at 10 mA cm⁻², which was identical with that used for the SEM observation. Beside the strong

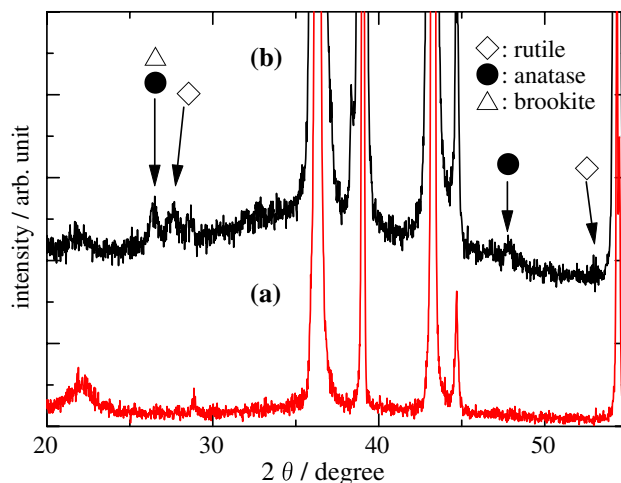


Fig. 3 XRD spectrum for the (a) HDG substrate before the electrochemical deposition and (b) HDG with TiO₂ film

peaks for the zinc layer on the HDG substrates, additional peaks that were not in the spectrum for the sample before the electrochemical deposition are seen in the TiO₂ deposited sample. These are attributable to the anatase, rutile and brookite structures of TiO₂ crystals, implying that the TiO₂ film is a mixture of these three crystal structures.

Following the successful coating of 1 cm × 1 cm HDG substrates with *c*-TiO₂ by electrochemical deposition, the next step was to examine if this method was also valid for the larger 10 cm × 20 cm samples. Figure 4 shows the SEM photographs for each part (part I–IV) of the HDG substrate after the electrochemical deposition. The deposition time was 5 min, which is equivalent to 3 C cm⁻². *c*-TiO₂ layers form on the central parts II and III, but on the part I and IV only a few crystalline particles were seen. Using EDX measurements we confirmed that the layer on part I was very thin and that on part IV was thick but fragile.

In order to elucidate this phenomenon, the spatial electric field distribution was simulated by three-dimensional finite element calculations. The software used was HiPhi (Advanced Science Laboratory, Inc.). The sample electrode

Fig. 2 Surface morphologies of the TiO₂ films on the 1 cm × 1 cm (a) HDG plate and (b) CRS plate obtained at 60 °C from 0.1 M titanium potassium oxalate dehydrate aqueous solution containing 1 M hydroxylamine adjusted to pH 8. The current densities were 10 mA cm⁻² equivalent to the quantity of electricity of 5 C cm⁻²

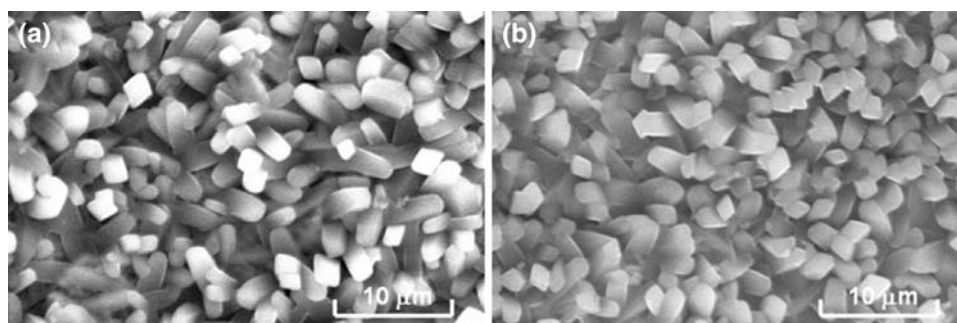
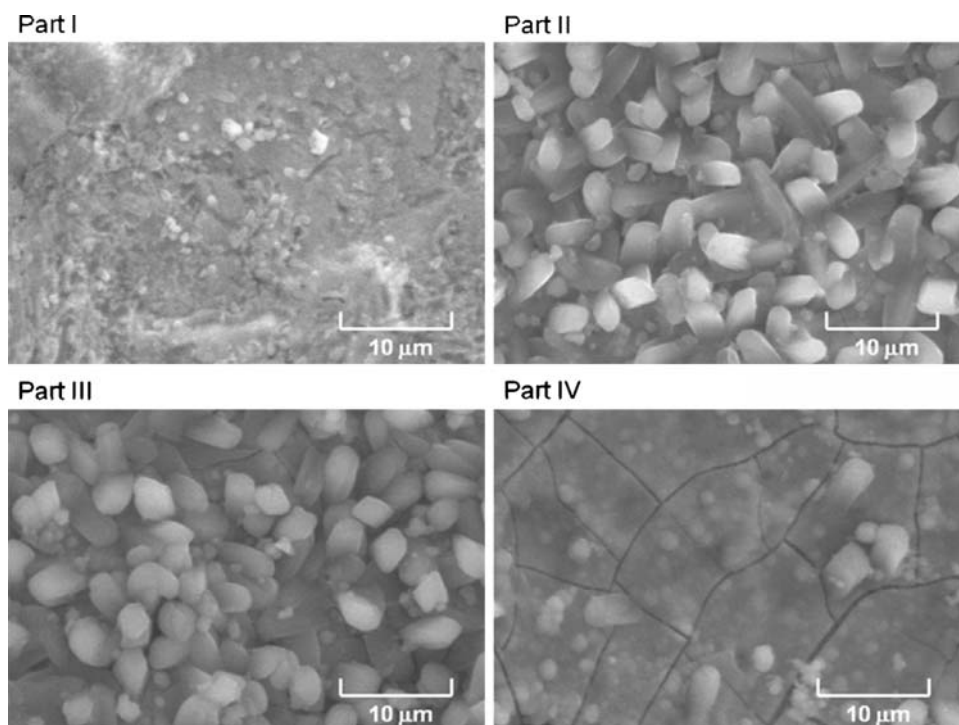


Fig. 4 Surface morphologies of the TiO₂ film on the 10 cm × 20 cm HDG plate. Part I–IV correspond to the area from the top edge: 3–4 cm (I), 8–9 cm (II), 13–14 cm (III) and 0–1 cm from the bottom edge (IV), respectively



and two counter electrodes were taken into account, and the electrolyte was assumed to be pure water. We neglected the effect of charged ions.

Figure 5 shows the result. The picture shows the electric field distribution on the plane perpendicular to the three electrodes and penetrating their centers. The local electric field around the bottom edge of the HDG sample electrode is much enhanced and the rest is almost uniform. The non-homogeneity of the electric field in this simulation was slightly exaggerated since the screening effect of the charged ions in the electrolyte was neglected. Nevertheless the simulation clearly explains that a thick amorphous film is formed on part IV because the current density around it is too high to form c-TiO₂. The thin amorphous layer on part I is probably due to the strong attraction of the charged ions to part IV by the electric field effect, which was weaker around part I.

To support this simulation, depositions with various current densities from 5 to 30 mA cm⁻² were performed (the electrolyte composition was the same). SEM measurements confirmed that crystalline layers formed in every part, but dependent on different current densities. On part I, a crystalline layer appeared at 15–20 mA cm⁻², but on parts II and III occurred only at 8–10 mA cm⁻². The crystalline layer appeared on part IV only at current density values smaller than 8 mA cm⁻². This clearly shows that the difference in morphology of each part is due to the different local current densities.

In order to overcome this difficulty, we canceled out the differences in the electrochemical deposition by applying

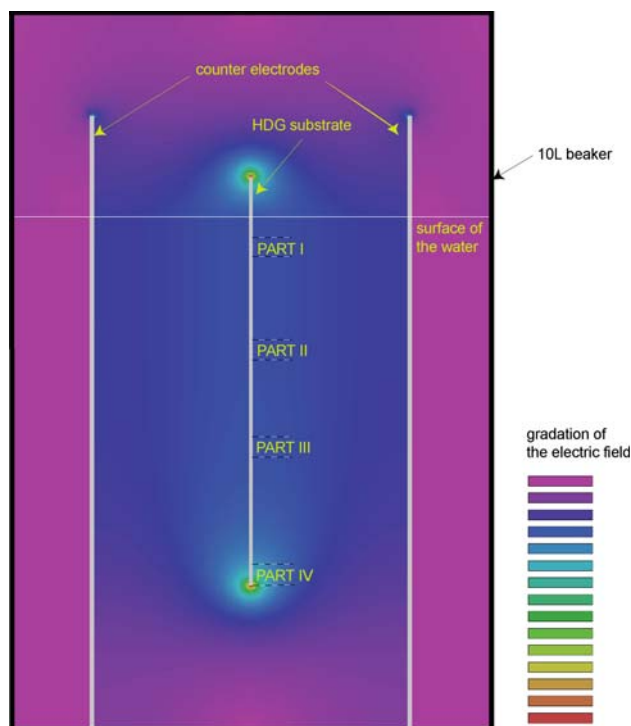
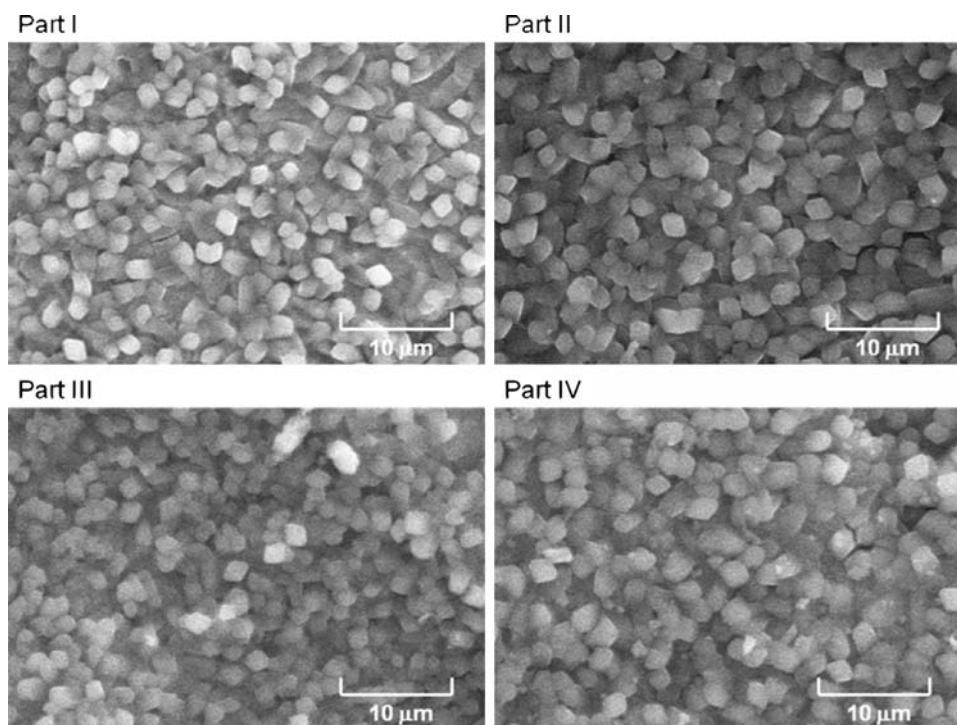


Fig. 5 The simulated spatial electric field distribution around the electrodes

three different current densities (5 mA cm⁻² (2 min), 10 mA cm⁻² (2 min), 20 mA cm⁻² (1 min) (totally 3 C cm⁻²)) continuously so that the crystalline layer forms in every part under one of the specific current densities.

Fig. 6 Surface morphologies for each part of the HDG substrate after electrochemical deposition with three different current densities applied continuously as 5 mA cm^{-2} (2 min), 10 mA cm^{-2} (2 min) and 20 mA cm^{-2} (1 min)



The result is shown in Fig. 6. The film was observed to be crystalline in all areas. In order to compare the film thickness of each part, EDX measurements were performed over a scan area ($\sim 50 \mu\text{m}$) much larger than the size of the rods. The film thicknesses were compared by the amount of Ti compared to Zn and Fe. Table 1 shows the relative atomic fractions among Ti, Zn and Fe (It was not possible to estimate the amount of oxygen because the energy of the specific X-ray of oxygen was too small to be detected by the apparatus). The fraction of Ti to Zn was almost the same everywhere showing that the film thickness was almost uniform.

Electrochemical deposition with a staged pulse current is always effective for any shaped target. The standard way to solve the problem of non-homogeneous coatings is to change the geometry of the counter electrode and to increase the number of connections to the lead line. However, it is usually difficult to predict the effectiveness of these methods without experimental validation. The present method is a useful tool for the uniform coating of

c-TiO₂ films onto large plates or complex shaped materials by using it complementarily with standard methods.

4 Conclusion

A crystalline TiO₂ film was electrochemically formed on $1 \text{ cm} \times 1 \text{ cm}$ HDG plates from a 0.1 M titanium potassium oxalate dehydrate aqueous solution containing 1 M hydroxylamine adjusted to pH 8 with KOH aqueous solution. The electrochemical deposition was performed galvanostatically at $60 \text{ }^\circ\text{C}$ without subsequent heat treatment. The same conditions were applied to larger $10 \text{ cm} \times 20 \text{ cm}$ HDG plates without success. Crystalline layers were seen only in the middle area, whereas the upper and the edge areas became amorphous.

However, this problem was overcome and a uniform coating of a c-TiO₂ layer was successfully realized by application of a staged pulse current (5 mA cm^{-2} (2 min), 10 mA cm^{-2} (2 min) and 20 mA cm^{-2} (1 min)).

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Table 1 Relative atomic fractions of Ti, Zn and Fe for each part of the HDG substrate determined by EDX

Part	Ti	Zn	Fe
I	24.04	74.19	1.78
II	33.0	65.11	1.89
III	30.92	66.98	2.1
IV	28.74	70.54	0.72

Unit: at.%

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