

Toner Mask Method for Imaging on Niobium

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Abstract

An anodized niobium (Nb₂O₅) layer on a niobium (Nb) plate makes various colors. A driving force of the coloration is considered to be the thin film interference between the Nb₂O₅ layer and the Nb plate. In this study, we explore the possibility that a toner mask method could be used for preparing a digital image on the Nb plate by an anodization. And we tried to erase the image on the Nb plate. We found that 1% hydrofluoric acid solution is able to erase the image, although a ghost image appeared. We also explored how to prevent the ghost image appearance.

1. Introduction

Niobium (Nb) is expected as a biocompatible material due to its chemical stability. In that case, adding information on Nb surface is needed for preventing errors. However carving on the surface may reduce its strength and/or cause health problems.

In the present work, we explored how to make images on a Nb plate on its surface using thin film interference. The target is to make two-dimensional barcode image on Nb surface without carving. Several metal films, including Nb, titanium exhibit various colors because of the thin film interference of passive layer [1-2]. Recently we reported the optical properties of the Nb₂O₅ coloration [3-4].

Mask method is a primitive one for making images on the metal surface. A mask substance on the metal surface set as images prevents anodization occurrence. After the mask substance is removed, as a result we get images on the metal surface. We think there are three desirable conditions for the imaging mask.

1. Easy to be set as image.
2. Durability against a reaction liquid for coloration.
3. Easy to be removed.

We investigated how to use toner for the laser beam printer as the mask substance [5]. We call it the toner mask method, and we think that the toner mask method has the desirable conditions above. And we tried to update the information on Nb surface by removing Nb₂O₅ layer chemically for an information update.

2. Experiment

2.1 Making a toner mask on a Nb plate

0.1mm thickness Nb plate (Nilaco Co., Ltd.) was used. A typical procedure in order to make a toner mask on the Nb plate was carried out as almost same as the one in the recent report [5].

At first, the Nb plate was cut into 20 x 20mm size. The toner mask image was printed on a cellophane taped gloss coated paper with only a black toner by Canon LBP-7010C. We used four types of images. Black solid image for durability tests (Figure 1). QR code image for the example of actual image (Figure 2). URL of the information center of Tokai University (<http://www.cc.u-tokai.ac.jp/>) was encoded in this QR code by

Psytec QR Code Editor Ver. 2.43. The numerical number mask pattern for 1st writing (Figure 3) and 2nd writing (Figure 4).



Figure 1. Black solid toner mask for durability check.



Figure 2. QR Code toner mask pattern.

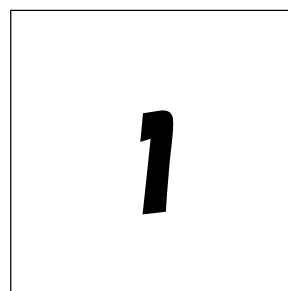


Figure 3. Numerical number mask pattern for 1st writing.

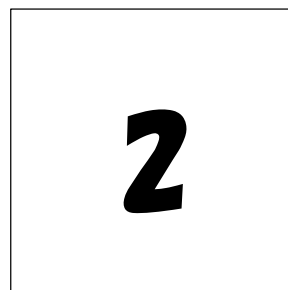


Figure 4. Numerical number mask pattern for 2nd writing.

The toner image printed on the gloss coated paper was thermally pressed to be transferred on the Nb plate surface at pre-determined temperature and pressure between supporting papers (Figure 5). In this study, 105 °C and 30kPa were set with a laminator (CLA402, Acco brands japan Co.). PPC paper (70gsm) was used as supporting papers.

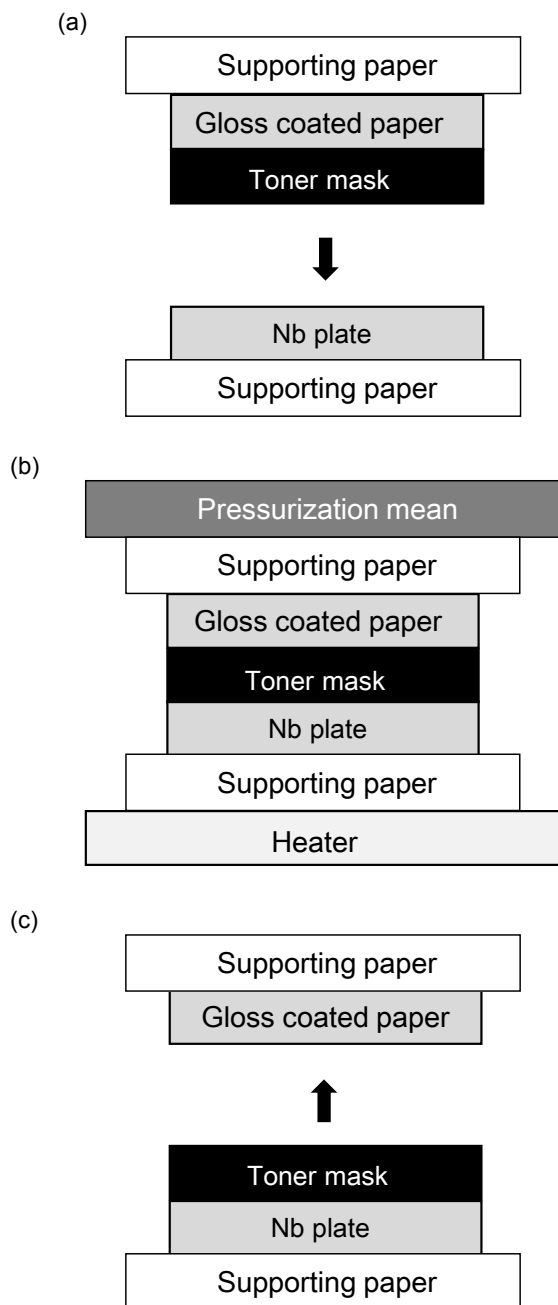


Figure 5. Schematic diagram of toner transfer to the Nb plate. (a) Before contact, (b) Heating and pressuring Toner mask on the Nb plate, (c) Separating the gloss coated paper.

2.2 Toner mask durability check

For checking a durability of the toner mask on a Nb plate, we tested 3 type samples. After the solid toner image was transferred on the Nb plate, (a) no processed sample, (b) 10% HNO_3 aqueous solution and (c) 1% HF aqueous solution were prepared. We checked the appearance of samples, and in order to make a quick check on the adhesiveness of the toner mask, cross-cut tests were performed. According to JIS K5600-5-6 (ISO2409), we made scratch pattern on the toner mask on the samples, then taped on the scratch pattern.

2.3 Making an image on a Nb plate

The first writing procedure was carried out as follows: The Nb plate with the toner mask was dipped into 100ml of 5.0w/v% citric acid solution (Wako Pure Chemical Industries, Ltd.) as the anode electrode (Figure 6).

A platinized titanium electrode was utilized as the cathode and the citric acid solution was utilized as electrolyte. The coloration voltage applied in 1 minute was +20V. An oxidized layer was formed on the surface of the Nb plate and the surface color changed blue. The Nb plate was then picked up, rinsed by an acetone to remove the toner mask.

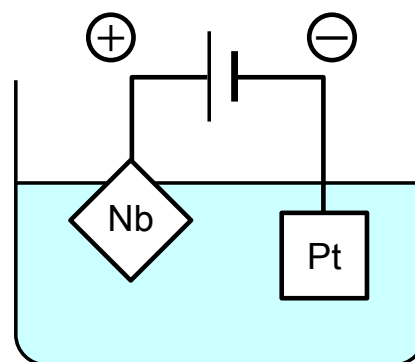


Figure 6. Schematic diagram showing the coloration of the Nb plate by anodization in a 100 ml of a 5.0 w/v% citric acid solution.

2.4 Erasing the image on the Nb plate and rewriting an another image

We tried to erase the image on the Nb plate by a chemical dissolution process. The Nb plate was dipped into 1% hydrofluoric acid (HF) solution to erase the images on its surface. In this case, to obtain a rewritable Nb plate, all area of Nb plate should be processed with the anodization at higher voltage than one for its coloration to prevent the appearance of ghost image before erasing which is explained in results section.

A typical procedure in order to obtain a rewritable Nb plate was carried out as follows: Before erasing the image, all area of the Nb plate should be processed by the anodization at +30V in 1 minute to avoid the appearance of ghost image.

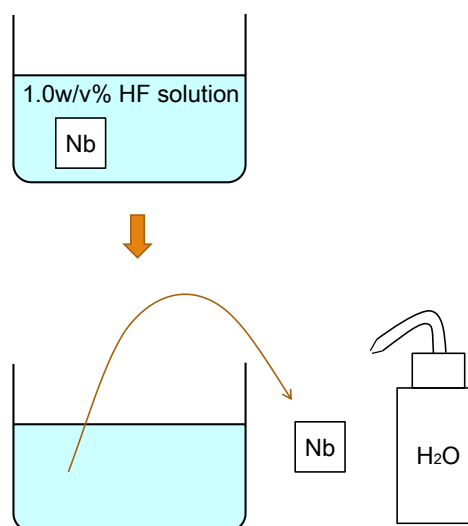


Figure 7. Schematic diagram showing the chemical erasing process.

The Nb plate was dipped into 1% HF solution (Kanto Chemical Co., Ltd.) in 2 hours to erase the image on its surface at a room temperature because Nb₂O₅ has strong chemical stability. During the Nb plate dipping into the 1% HF solution, air bubbles occurred on its surface. Then the plate was picked up, rinsed by pure water (Figure 7).

Rewriting means the second writing on the Nb plate whose first image had been erased. The second writing procedure was almost same as the first writing one. To distinguish from the first writing, the numerical number mask pattern for 2nd writing was used.

3. Results and discussion

3.1 Toner mask durability check

An example of a cross-cut result is shown in Figure 8. And durability test results were summarized in Tables 1 and 2. All toner mask appearance didn't change after dipping any solutions. All samples showed good adhesion behavior to Nb plates. We think that the black toner mask of LBP-7010C were strong against water and acid solution.

On the other hand, organic solvent, like acetone or methyl ethyl ketone, could solve the toner mask easily. Also the toner mask was weak for the mechanical stress, for example a sharp needle could break the mask.

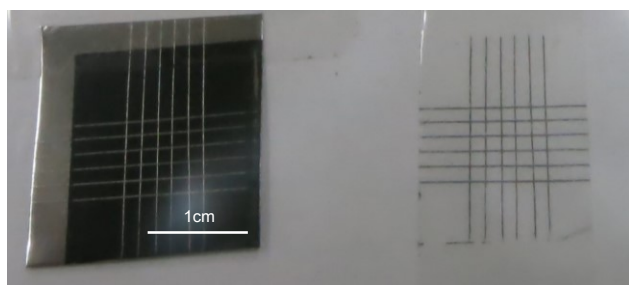


Figure 8. An example of a cross-cut test result.

Table 1. Durability test results of the toner mask appearance.

No processed	10% HNO ₃	1% HF
-	Unchanged	Unchanged

Table 2. Durability test results of the toner mask by cross-cut tests.

No processed	10% HNO ₃	1% HF
Rank 0	Rank 0	Rank 0

Rank 0 means almost no separation.

3.2 Making image on a Nb plate

The toner masked Nb plate was shown in Figure 9, then the Nb plate was anodized (Figure 10). The color of none-masked area of the Nb plate changed blue at the first writing. And then the mask toner was removed, image on the Nb plate surface was recognized (Figure 11). We conclude that the black toner mask of LBP-7010C was effective for Nb plates by the anodization imaging.

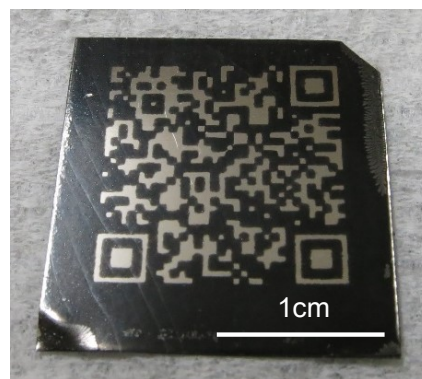


Figure 9. Toner masked, before coloration.

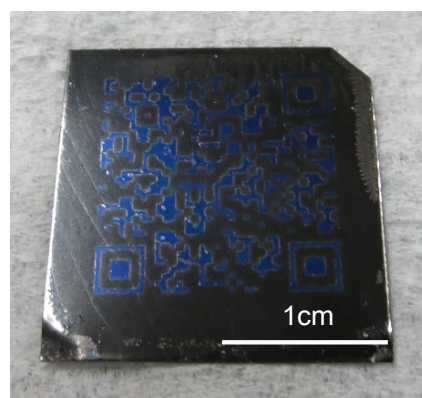


Figure 10. After coloration at +20V, before the toner mask removed.

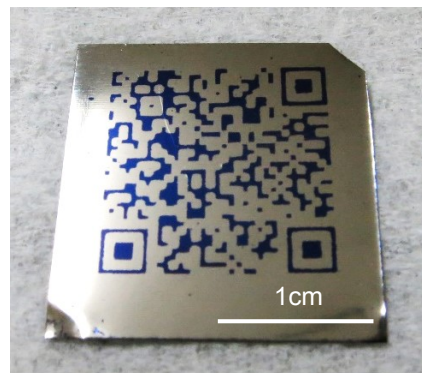


Figure 11. Removed the toner mask with acetone.

3.3 Erasing and rewriting image on a Nb plate

The image on a Nb plate was prepared, then this sample was dipped into 1% HF solution simply, the last image was still observed on the processed surface (Figure 12). We call it a ghost image. We thought that the ghost image appeared because colored area and non-colored area changed to different colors when they had been dipped into 1% HF solution.

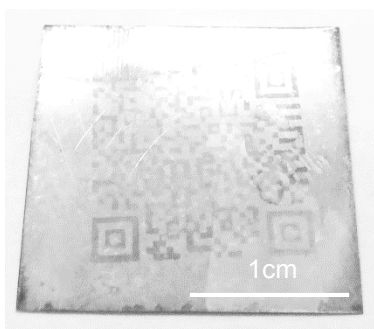


Figure 12. Ghost image appeared sample.

In order to avoid the appearance of the ghost image, it was needed that all area of sample was made into the same color before erasing. For this test, the numerical mask patterns were used.

At first, the numerical image “1” was written on the Nb plate surface (Figure 13). Then we applied +30V, which was a higher voltage relative to the coloration voltage (+20V) on all area of the Nb plate before dipping into the 1% HF solution (Figure 14). Apparently the ghost image disappeared from the image erased surface (Figure 15). And we were able to make another numerical image “2” on the erased Nb plate surface by the same method as the first writing (Figure 16).

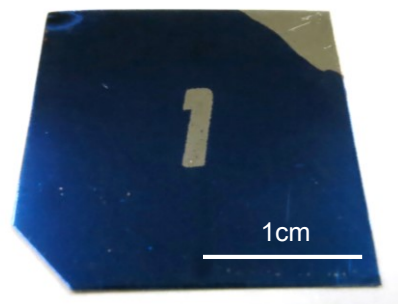


Figure 13. Before erasing 1st imaging on the Nb plate..

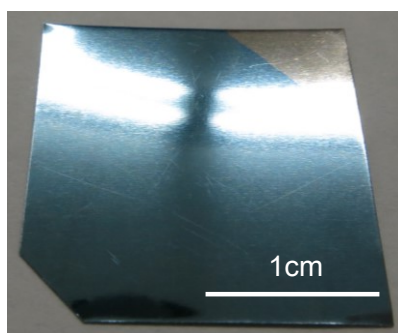


Figure 14. After the higher voltage (+30V) than the coloration voltage (+20V) was applied.

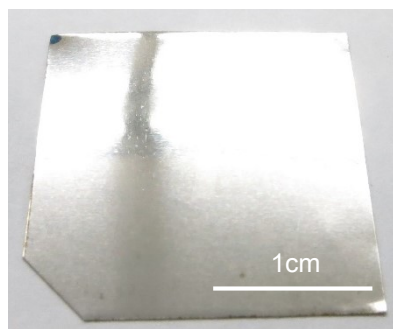


Figure 15. After 1st image erased.

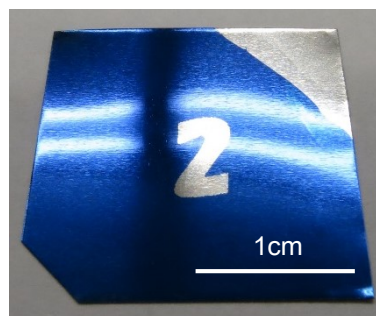


Figure 16. After 2nd writing.

4. Conclusions

We were able to make an image on a Nb plate by the anodization with the toner mask method and erase it by the chemical dissolution process. We found that adding a higher voltage relative to that of the coloration prevented the ghost image appearance at the erasing process. And we were able to make another image on the Nb plate.

References

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Author Biography

Isao Komatsu is a Ph.D. candidate of Tokai University. He received his M. Eng. degree in applied chemistry from Waseda University in 2001. His current research interests include imaging materials and printing devices.