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Change of Morphology of Titanium Surface by Pickling in Nitric-Hydrofluoric Acid Solutions



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Abstract

Accompanying the expanding use of titanium, various qualities have been in demand for the product surfaces. Above all, from a viewpoint of landscapes and designs antiglare, quality is required for roofs and walls of buildings. Authors have noticed dissolving product surfaces by nitric-hydrofluoric acid solutions to obtain dull surfaces and examined the effects of the solution composition (concentrations and metal contaminants) on surface morphologies, glossiness and whiteness. In the case of constant hydrofluoric acid concentrations, the glossiness decreases and the whiteness increases as nitric acid concentration is lower because roughness increases due to unevenness formation that is the same size with grains. In opposition with increasing nitric acid concentration and iron contaminant from stainless steels the surfaces of titanium, products become smooth and therefore their glossiness increase. These effects are thought to be due to depressing the anisotropy of titanium solution velocity by both nitric acid and contaminants from stainless steels.

1. Introduction

Titanium is used in many civilian goods, including building members, mufflers of large motorcycles and mugs, by making use of its excellent corrosion resistance and high specific strength (light weight). Titanium is consequently demanded to meet diversifying surface quality requirements. On the building roofs and walls where titanium is used over large areas, antiglare quality and antiglare uniformity are required of titanium[1-5]. The antiglare quality of titanium can be effectively improved by the formation of minute surface irregularities that diffusely reflect light. The surface morphology of titanium can be adjusted by mechanical methods, such as transferring surface patterns of the mill-roll and projecting blast particles, or by chemical methods like acid pickling[1-5]. The most general method of dissolving titanium is pickling in a nitric-hydrofluoric acid solution (a mixture of nitric acid and hydrofluoric acid solutions). Many studies have been published on the dissolution reaction and reaction rate of nitric-hydrofluoric acid pickling[6], but few detailed reports are available on the change in the surface morphology of titanium with nitric-hydrofluoric acid pickling[5].

This article reports the results of the study the authors conducted on the effect of the nitric-hydrofluoric acid solution composition (con-

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centration and other metals), centering on the changes in the surface morphology, glossiness, and whiteness of titanium with nitric-hydrofluoric acid pickling.

2. Experimental Methods

Cold-rolled and annealed sheets of JIS Grade 1 commercially pure titanium were dipped in nitric-hydrofluoric aid solutions under various conditions. The surface morphology of the pickled titanium sheets was observed by optical microscopy, and their glossiness Gs45 and whiteness (brightness) L* were investigated as indexes of surface roughness and antiglare quality. Gs45 is a value measured by the method 4 of JIS Z 8741, using a Nippon Denshoku Model VG-1D digital variable-angle gloss meter. It corresponds to reflectivity when the angle of incidence and the angle of light reception are both 45°. Specular glossiness is 1,000%. L* is a value that indicates brightness or whiteness in the L*a*b* color system of JIS Z 8729 and was measured with light source C using a Minolta Model CR-200b colorimeter. The L* value of white paper is about 95. The smaller the Gs45 value, the lower the gloss, and the larger the L* value, the higher the whiteness. This agrees with the impression received with the naked eye. The dissolution amount of the titanium sheets in the nitric-hydrofluoric acid solution was determined from the weight change before and after nitric-hydrofluoric acid pickling.

3. Experimental Results

3.1 Effect of nitric acid concentration in nitric-hydrofluoric acid solution

Photo 1 shows the change in the surface morphology (optical micrographs) of titanium with the dipping time in the nitric-hydrofluoric acid solution when the hydrofluoric acid concentration was fixed at 45 g/l and the nitric acid concentration was changed. **Photo 2** shows surface optical micrographs and roughness profiles comprising: titanium after dipping in a nitric-hydrofluoric acid solution with a low nitric acid concentration of 20 g/l (a); titanium after dipping in a nitric-hydrofluoric acid solution with a high nitric acid concentration of 142 g/l (c); and austenitic stainless steel SUS 304 after dipping in a nitric-hydrofluoric acid solution. The specimens were commercially pure titanium sheets with a grain size of about 21 μm (grain size number of about 8.5) and surface polished to #600. The nitric-hydrofluoric acid solution temperature was 45°C.

In Photo 1, the nitric acid concentration increases toward the right, and the dipping time increases toward the bottom. Grains are clearly revealed initially when the specimen is dipped in the nitric-hydrofluoric acid solution. The individual grains appear more uneven as the dipping time increases or the nitric acid concentration decreases (toward the lower left of Photo 1 or as shown in Photo 2(a)), and appear smoother as the nitric acid concentration increases (toward the lower right of Photo 1 or as shown in Photo (b)). As shown in Photo 2(c), the austenitic stainless steel SUS 304 is preferentially dissolved at the grain boundaries when dipped in the nitric-hydrofluoric acid solution. This is clearly different from the surface morphology of titanium.

Fig. 1 shows the changes in the surface roughness Ra (a) and glossiness Gs45 (b) of titanium sheet specimens with the dissolution amount of titanium per sheet one-side when the titanium sheet specimens are dipped in nitric-hydrofluoric acid solutions with different nitric acid concentrations. As the dissolution amount of titanium increases with increasing dipping time as shown in Photo 1(a), the

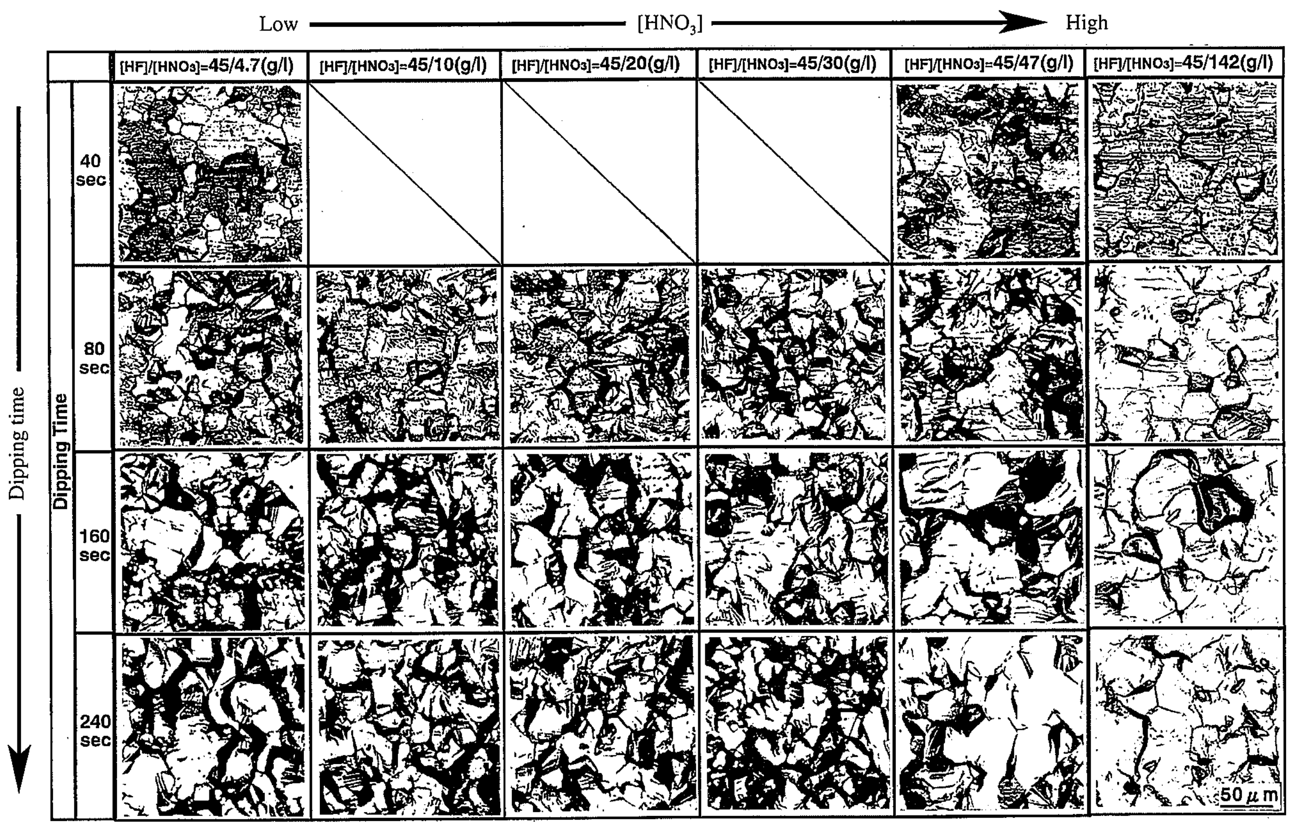
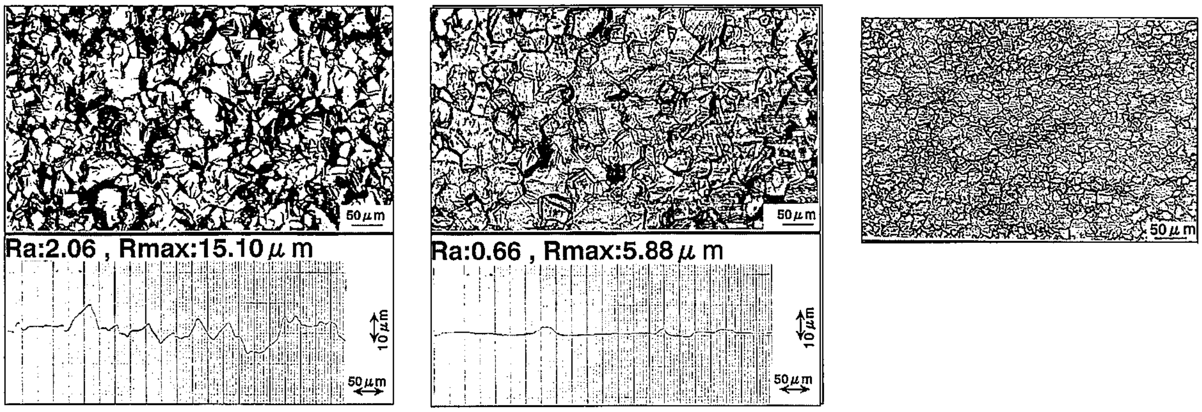


Photo 1 Change in surface morphology of titanium with dipping time when nitric acid concentration in nitric-hydrofluoric acid solution is changed (comparison of optical micrographs)



(a) Titanium after pickling in nitric-hydrofluoric acid solution (hydrofluoric acid concentration of 45 g/l and nitric acid concentration of 20 g/l)

(b) Titanium after pickling in nitric-hydrofluoric acid solution (hydrofluoric acid concentration of 45 g/l and nitric acid concentration of 142 g/l)

(c) Stainless steel SUS 304 (18Cr-8Ni) after pickling in nitric-hydrofluoric acid solution

Photo 2 Surface optical micrographs and roughness profiles of titanium (effect of nitric acid concentration)

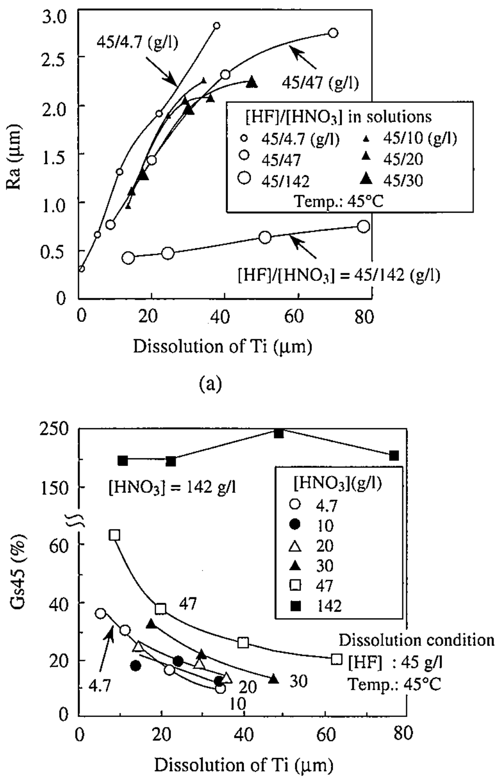


Fig. 1 Changes in surface roughness Ra (a) and glossiness Gs45 (b) of titanium with dissolution amount when titanium is pickled in nitric-hydrofluoric acid solutions with different nitric acid concentrations

surface roughness Ra changes little when the nitric acid concentration is the highest 142 g/l, markedly increases when the nitric acid concentration decreases, and reaches as much as about 2.0 μm when the dissolution amount is 20 to 30 μm (the specimens are dipped at 45°C for about 160 s). These conditions correspond to the surface morphology characteristics shown in Photo 1 and Photo 2. As shown in Fig. 1(b), the glossiness Gs45 remains practically constant at a high level of 200 to 250% when the nitric acid concentration is the highest 142 g/l, markedly decreases when the nitric acid concentration is lower, and reaches a lower 20 to 40% when the dissolution amount of titanium is 20 to 30 μm (the specimens are dipped at 45°C for 160 s). The surface roughness Ra and the glossiness Gs45 are related as shown in **Fig. 2**. As the surface roughness Ra increases, the glossiness Gs45 decreases.

The surface morphology of titanium greatly changes in this way with the nitric acid concentration of the nitric-hydrofluoric acid solution. When the nitric acid concentration is low (47 g/l or less) as shown in **Fig. 3**, the glossiness Gs45 is low and stable. The whiteness L* is high at 74 to 76 when the nitric acid concentration is 10 to 47 g/l. When the nitric acid concentration decreases too low to 4.7 g/l, brown staining occurs to decrease the whiteness L* to about 66. When the nitric acid concentration is the highest 142 g/l, the glossiness Gs45 is high or over 200%, and the whiteness L* is low or about 69. Decreasing the nitric acid concentration of the nitric-hydrofluoric acid solution increases the formation of irregularities on

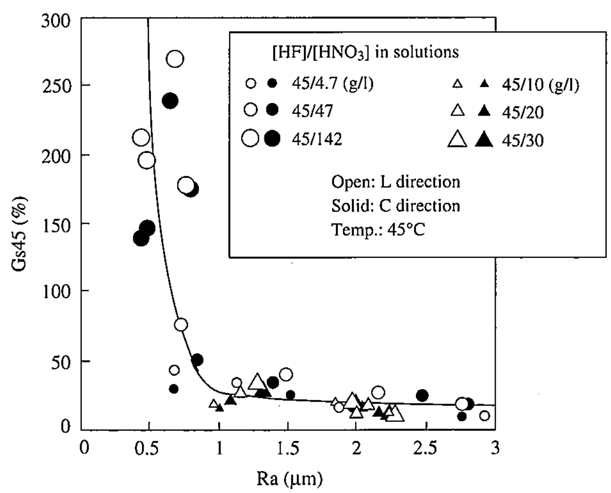


Fig. 2 Relationship between surface roughness Ra and glossiness Gs45 of titanium pickled in nitric-hydrofluoric acid solutions with different nitric acid concentrations

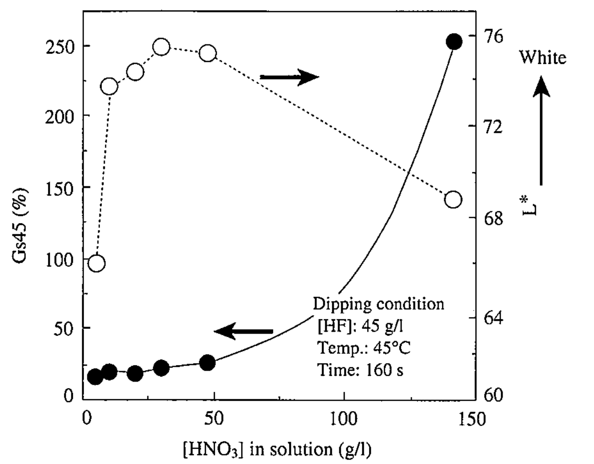


Fig. 3 Effect of nitric acid concentration in nitric-hydrofluoric acid solution on glossiness Gs45 and whiteness L* of titanium after pickling

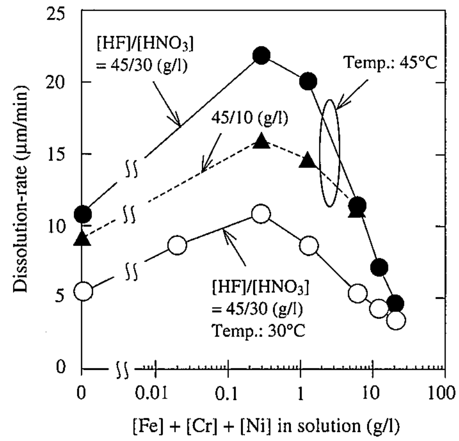


Fig. 4 Effect of stainless steel component concentration ([Fe] + [Cr] + [Ni]) on dissolution rate of titanium in nitric-hydrofluoric acid solution

an individual grain basis on the surface of titanium and provides titanium with surface appearance of low glossiness Gs45 and high whiteness L*.

3.2 Effect of stainless steel components in nitric-hydrofluoric acid solution

Titanium often shares a nitric-hydrofluoric acid pickling line with stainless steel. In such a case, stainless steel components, such as iron, nickel and chromium, are present in the nitric-hydrofluoric acid solution. This makes it necessary to determine the effect of the stainless steel chemical composition in addition to the nitric acid and hydrofluoric acid compositions. Mixing and adjusting nitric-hydrofluoric acid solutions in which stainless steel components were dissolved in large amounts, the present work evaluated the effects of the stainless steel component concentration (sum of component concentrations [Fe] + [Cr] + [Ni] = 0.03-21 g/l, component concentration ratio [Fe]:[Cr]:[Ni] = 10:2:1) and of the nitric acid concentration (0.5-30 g/l) on the surface morphology of titanium in a nitric-hydrofluoric acid solution with a constant hydrofluoric acid concentration of 45 g/l.

Fig. 4 shows the effect of the stainless steel component concentration ([Fe] + [Cr] + [Ni]) in the nitric-hydrofluoric acid solution on the dissolution rate (one-side dissolution amount/min) of titanium. The dissolution rate of titanium increases and nearly doubles as the stainless steel component concentration, mainly composed of iron, increases to 0.3 g/l. The dissolution rate of titanium gradually decreases with increasing stainless steel component concentration and becomes lower than in the absence of stainless steel components as the stainless steel component concentration increases above 6 g/l.

Photo 3 shows the effects of the stainless steel component concentration and the nitric acid concentration on the surface morphology (optical micrographs) of titanium. **Photo 4** shows the surface optical micrographs and roughness profiles of titanium sheet specimens when the stainless steel component concentration is low or 0.3 g/l (a) and high or 21.0 g/l (b) in the nitric-hydrofluoric acid solution (nitric acid concentration of 30 g/l and hydrofluoric acid concentration of 45 g/l). These results are concerned with the titanium sheet surfaces dipped in the solution at a temperature of 45°C for 80 s.

The nitric acid concentration increases toward the right of Photo 3, and the stainless steel component concentration decreases toward the bottom of Photo 3. Dipping in the nitric-hydrofluoric acid solution clearly reveals grains as shown in Photo 1. The individual grains increase in roughness with decreasing nitric acid concentration and stainless steel component concentration (toward the lower left of Photo 3 or as shown in Photo 4(a)), and increase in smoothness with increasing nitric acid concentration and stainless steel component concentration (toward the upper right of Photo 3 or as shown in Photo 4(b)).

Fig. 5 shows the effects of the stainless steel component concentration in the nitric-hydrofluoric acid solution on the surface roughness Ra (a) and glossiness Gs45 (b) of titanium. Fig. 5 gives the results obtained with three levels of titanium sheets (first with grain size number 9.3 and initial glossiness Gs45 of 475%, second with grain size number 9.3 and initial glossiness Gs45 of 70 to 80%, and third with grain size number 10.2 and initial glossiness Gs45 of 70 to 80%). The effects of the grain size and other factors described in another report are also included.

As can be seen from Fig. 5, increasing the stainless steel component concentration decreases the surface roughness Ra and increases the glossiness Gs45. The glossiness Gs45 increases as the surface roughness Ra decreases as shown in Fig. 2. Comparison is made between a low nitric acid concentration of 10 g/l (marked ○, △ and □ in Fig. 5) and a high nitric acid concentration of 30 g/l (marked ●, ▲ and ■ in Fig. 5). The low nitric acid concentration increases the surface roughness Ra and decreases the glossiness Gs45, or alleviates the effect of the stainless steel components. The glossiness Gs45 decreases (as described in another report) with increasing grain size number or decreasing grain size (marked ■ and □ in Fig. 5(b)). Increasing the stainless steel component concentration in the nitric-hydrofluoric acid solution increases the surface smoothness and glossiness Gs45 of titanium. Decreasing the nitric acid concentration alleviates the tendency for the stainless steel components to increase the surface smoothness and gloss of titanium.

4. Discussion

The surface morphology of commercially pure titanium after pickling in a nitric-hydrofluoric acid solution changes with the nitric acid concentration and stainless steel component concentration in the nitric-hydrofluoric acid solution as described above. These changes can be clearly grasped as differences in the surface roughness Ra, glossiness Gs45, and whiteness L*. **Fig. 6** schematically illustrates the effects of the nitric acid and stainless steel component concentra-

Conditions: HF = 45 g/l, Solution temperature: 45°C, Dipping time: 80 s

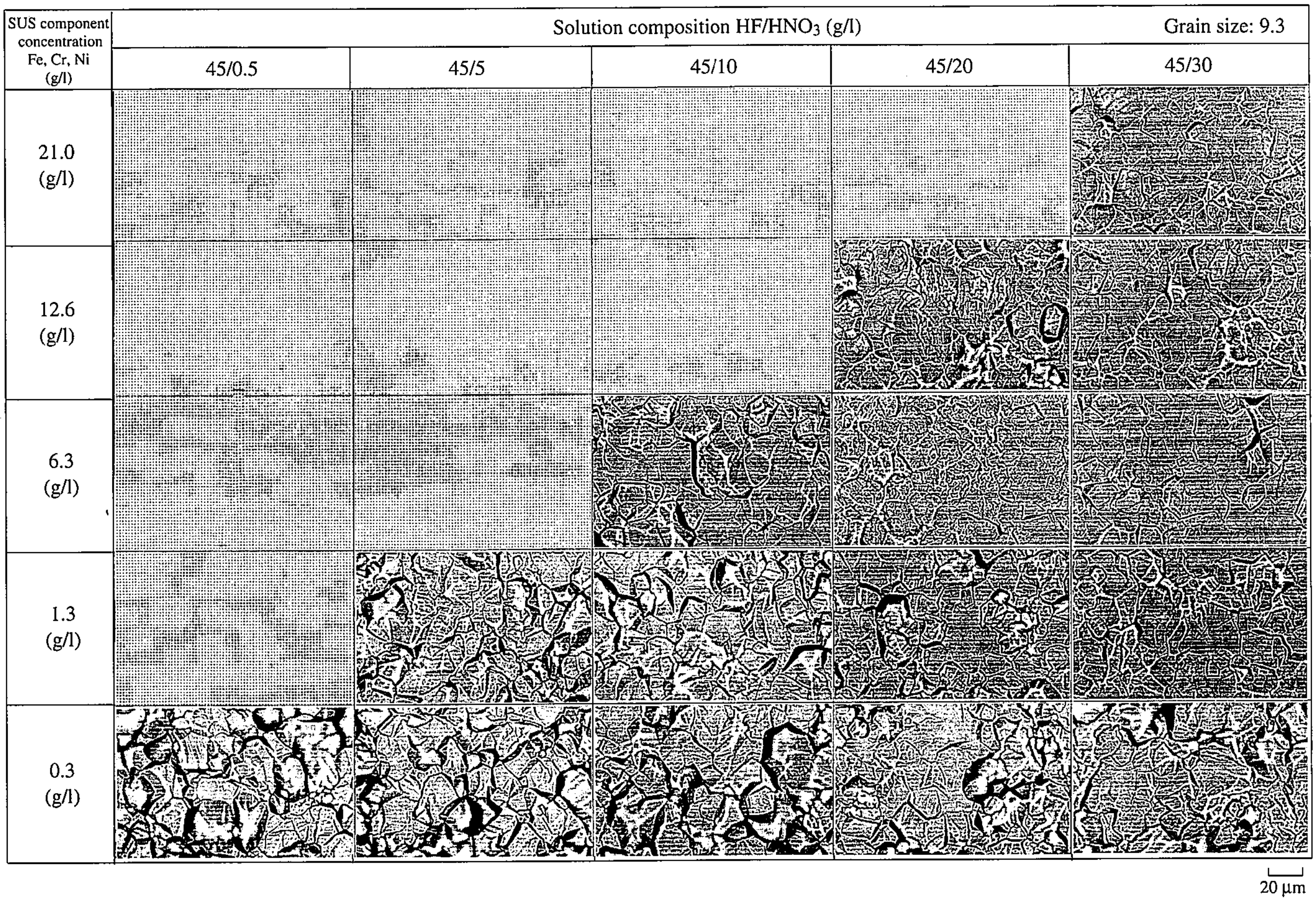


Photo 3 Effects of stainless steel component concentration ([Fe] + [Cr] + [Ni]) and nitric acid concentration in nitric-hydrofluoric acid solution on surface morphology of titanium (optical micrographs)

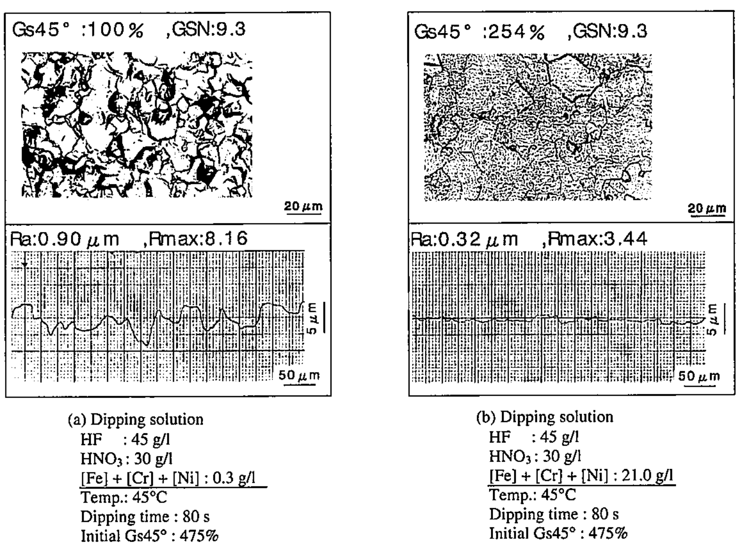


Photo 4 Surface light micrographs and roughness profiles of titanium (effect of stainless steel component concentration) when stainless steel component concentration ([Fe] + [Cr] + [Ni]) in nitric-hydrofluoric acid solution (hydrofluoric acid concentration of 45 g/l and nitric acid concentration of 30 g/l) is 0.3 g/l (a) and 21.0 g/l (b)

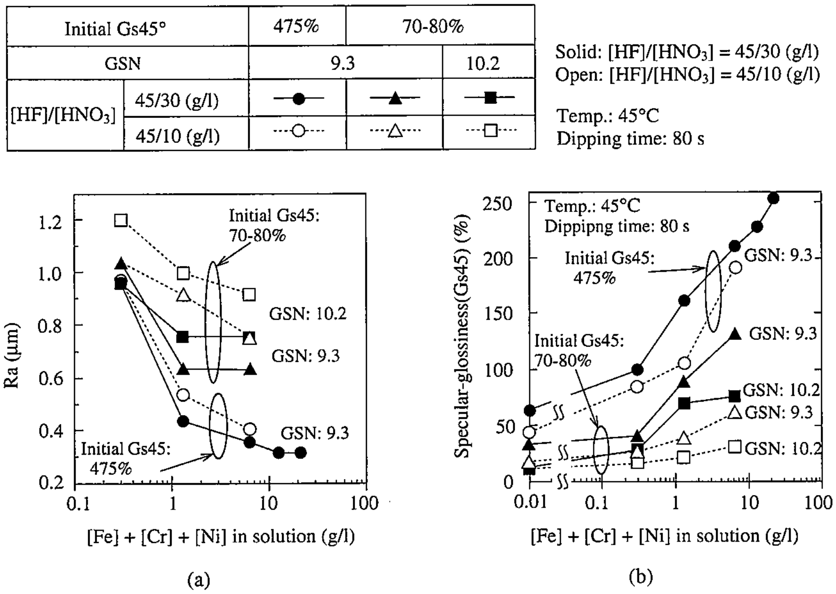


Fig. 5 Effects of stainless steel component concentration ([Fe] + [Cr] + [Ni]) in nitric-hydrofluoric acid solution on surface roughness Ra (a) and glossiness Gs45 (b) of titanium after pickling (effects of grain size and initial glossiness also included)

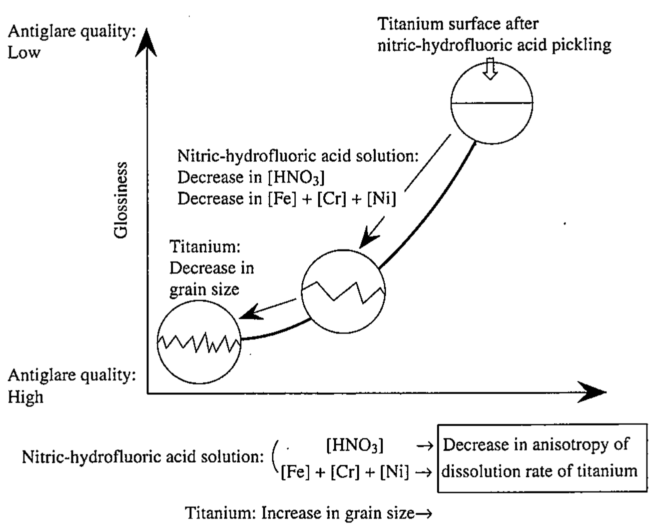


Fig. 6 Factors that affect surface morphology and glossiness (antiglare quality) of titanium

tions in the nitric-hydrofluoric acid solution on the surface morphology and glossiness (antiglare quality) of titanium. When titanium is pickled in hydrofluoric acid, surface irregularities are formed on an individual grain basis because the dissolution rate depends on the crystal orientation and is anisotropic. As the nitric acid or stainless steel component concentration increases, the anisotropy of the dissolution rate is reduced and considered to increase the surface smoothness of titanium.

To enhance the antiglare property of titanium as required for building applications, minute surface irregularities that diffusely reflect light must be formed to reduce the glossiness of titanium. When the nitric acid concentration or stainless steel component concentration is high in the nitric-hydrofluoric acid solution, the titanium is smooth surfaced, high in glossiness, and low in antiglare quality (toward the upper right of Fig. 6). Decreasing the nitric acid concentration or stainless steel component concentration forms surface irregularities on an individual grain basis, with the result that the titanium decreases in glossiness and increases in antiglare quality (toward the lower left of Fig. 6). As the grain size of titanium itself is reduced, the number of surface irregularities per unit length increases to decrease smooth portions, which in turn reduces further the glossiness of titanium. In this way, the nitric acid and stainless steel components are considered to act to alleviate the anisotropy of the dissolution rate with respect to the dissolution phenomena of titanium in the nitric-hydrofluoric acid solution. Since iron ions act as oxidizer to make the corrosion potential of titanium more noble in the same way as nitric acid, an oxidizing acid, does[7], a correlation with the corrosion potential is presumed.

In the relationship between the stainless steel components and the dissolution rate of titanium shown in Fig. 4, trace iron ions raise the cathode current and add to the corrosion potential of titanium. As a result, the dissolution current of titanium increases, probably increasing the dissolution rate. The reduction of the dissolution rate by the stainless steel components is probably due to the adsorption and precipitation of stainless steel component ions on the surface of titanium, which in turn inhibit the dissolution of titanium. When copper ions are present in large amounts in the nitric-hydrofluoric acid solution, copper sometimes precipitates on the surface of titanium and forms pits in the surface of titanium.

Below is discussed the relationship between the surface morphology and whiteness L* of titanium. When attention is focused only on the surface morphology of titanium, excluding its interference color and object color, its whiteness is enhanced when visible rays are scattered. When random irregularities of the order of visible ray wavelength (1 μm or less) are formed on the surface of titanium, the whiteness L* is increased. If there are minute irregularities on an individual grain basis, the whiteness L* is enhanced. Since extremely fine irregularities are also effective, the whiteness L* remains high except when the nitric acid concentration is high and the surface is smooth (Fig. 3). When the nitric acid concentration is very low, brown staining occurs probably because the insufficiency of nitric acid, an oxidizing acid, reduces the oxidizing power to such a degree that titanium, a colored material, forms corrosion products of the valence +2 or +3[7-9].

5. Conclusions

The change in the surface morphology of cold rolled and annealed sheets of JIS Grade 1 commercially pure titanium with nitric-hydrofluoric acid pickling was studied, centering on the effects of the nitric acid concentration and stainless steel components (metal components) in the nitric-hydrofluoric acid solution on the surface morphology, surface roughness, glossiness, and whiteness of titanium. The following conclusions were obtained:

(1) When the nitric-hydrofluoric acid solution has a constant hydrofluoric acid concentration of 45 g/l and a low nitric acid concentration of 47 g/l or less, it forms noticeable irregularities on an individual grain basis on the surface of titanium and increases the surface roughness of titanium. As a result, the glossiness Gs45 decreases to 20 to 40%, and the whiteness L* increases to 74 to 76. When the nitric acid concentration is the highest 142 g/l, the surface of titanium is smooth, the glossiness Gs45 exceeds 200%, and the whiteness L* declines to about 69.

(2) When the stainless steel component concentration, mainly composed of iron, increases in the nitric-hydrofluoric acid solution, the stainless steel components act like the nitric acid noted in (1) above, and increase the surface smoothness and glossiness of titanium.

(3) The nitric acid and stainless steel components are oxidizing and reduce the anisotropy of the dissolution rate of titanium. Decreasing the nitric acid concentration and stainless steel component concentration forms irregularities on an individual grain basis on the surface of titanium. These minute surface irregularities diffusely reflect light, decrease the glossiness of titanium, and increase the antiglare quality of titanium.

(4) The whiteness L* is enhanced as visible rays are scattered by random surface irregularities of the order of visible ray wavelength (1 μm or less). Extremely minute irregularities also have the action of enhancing the whiteness L*. The whiteness L* of titanium is thus stabilized relatively high, except when the nitric acid concentration is high and the surface is smooth.

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