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Effect of Grain Size and Initial Surface Condition on Glossiness and Whiteness of the Pickled Titanium Surface




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Abstract

Titanium has been applied to roofs and walls of buildings due to its high corrosion resistance. Antiglare qualities have been in demanded with regard to its application. The dissolution of product surfaces by the nitric-hydrofluoric acid solutions is known as the way to improve the surface finish for reducing glare. The authors have investigated the effects of the grain size and initial surface conditions on the glossiness and the whiteness of the dissolved titanium surface. Consequently, with decreasing grain sizes the unevenness of the surfaces becomes fine and the glossiness decreases because the unevenness with the same size as that of grains is formed. The effects of the initial surface conditions on the glossiness are different according to the grain sizes. In the case of coarse grains, glossiness remains constant because the unevenness of the dissolved surfaces is nearly equal to its initial state. However, in the case of fine grains, fine unevenness by dissolving plays a dominant role in glossiness. The whiteness increases sharply by short dipping in the mixed acid regardless of initial surface conditions.

1. Introduction

Titanium has such excellent corrosion resistance so it is used in the roofs and walls of buildings that exist in severe environments, such as coastal and volcanic regions. The reasons for the use of titanium in such regions are its esthetic appearance and image in addition to its economics resulting from high corrosion resistance and consequently low long-term maintenance cost. Its antiglare quality is especially required of titanium from the standpoints of landscape and esthetic appearance[1-5]. The antiglare quality of titanium is generally evaluated by its glossiness and whiteness (brightness), and improves with decreasing glossiness and increasing whiteness. Pickling in a nitric-hydrofluoric acid solution (a mixture of nitric and hydrofluoric acid solutions) is a well-known method for improving the antiglare quality of titanium by forming minute irregularities on the surface of titanium. The effects of the acid and metallic component concentrations in the nitric-hydrofluoric acid solution and of the grain size and oxide scale of titanium on the antiglare property of

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titanium are already reported[6-8]. This article describes how the differences in the grain size and initial surface condition (before nitric-hydrofluoric acid pickling) affect the glossiness and whiteness of titanium after nitric-hydrofluoric acid pickling.

2. Experimental Methods

First, to investigate the effect of grain size, cold-rolled and annealed sheets of JIS Grad 1 commercially pure titanium with different grain size numbers (GSNs) were surface finished to #600 and were dipped in nitric-hydrofluoric acid solutions under different conditions.

Then, four types of commercially pure titanium sheets with different grain sizes and different levels of surface glossiness and roughness ((a) low glossiness and coarse grain size, (b) high glossiness and coarse grain size, (c) low glossiness and fine grain size, and (d) high glossiness and fine grain size in **Table 1**) were dipped in nitric-hydrofluoric acid solutions under different conditions. The surface glossiness and roughness of the commercially pure titanium sheets were adjusted by lightly cold rolling them and transferring dull roll finish onto them.

The surface morphology of titanium sheet after nitric-hydrofluoric acid pickling was observed by optical microscopy, and the glossiness Gs45 and whiteness (brightness) L* that become indexes of surface roughness and antiglare quality of titanium, respectively, were investigated. The glossiness Gs45 was measured with a Nippon Denshoku Model VG-1D digital variable-angle gloss meter by the method 4 of JIS Z 8741. It corresponds to reflectivity when the angle of incidence and the angle of light reception are both 45°. Specular glossiness is 1,000%. The whiteness L* indicates brightness or whiteness in the L*a*b* color system of JIS Z 8729, and was measured with light source C by using a Minolta Model CR-200b colorimeter. The whiteness L* of white paper is about 95. The lower the glossiness Gs45, the less glossy the titanium surface appears, and the higher the whiteness L*, the whither the titanium surface appears. This agrees with how the titanium sheet appears to the naked eye.

3. Experimental Results

3.1 Effect of grain size (or grain size number)

The titanium sheets were surface finished to #600 and dipped in nitric-hydrofluoric acid solutions with a constant hydrofluoric acid concentration of 45 g/l and a variable nitric acid concentration of 10 to 30 g/l. The effect of the grain size (or grain size number) on the glossiness Gs45 of the titanium sheets after dipping in the nitric-hydrofluoric acid solution is shown in **Fig. 1**. The glossiness Gs45 decreases with increasing grain size number or decreasing grain size. The difference in the glossiness Gs45 with the nitric acid concentration in the nitric-hydrofluoric acid solution[6] decreases with increasing grain size number or decreasing grain size, and practically disappears when the grain size number exceeds 9.

The relationship between the surface roughness Ra and glossiness Gs45 of the titanium sheets after dipping in the nitric-hydrofluoric acid solution is shown in **Fig. 2**. A distinction can be made between the grain sizes of 9 and 21 μm. When the grain size is 9 μm, the surface roughness Ra varies over 1.0 μm, but the glossiness Gs45 varies by only 10% and is stable. When the grain size is 21 μm, the glossiness Gs45 decreases as the surface roughness Ra increases. The nitric-hydrofluoric acid solution used here is low in the nitric acid concentration and is of such a composition as to form irregularities on an individual grain basis on the surface of titanium[6]. The surface morphologies of two titanium sheets are shown in **Photo 1**. When the two are compared at the same magnification, the titanium sheet with the grain size of 9 μm (Photo 1(b)) has shallower and finer surface irregularities. According to its surface roughness pro-

Table 1 Glossiness Gs45, whiteness L*, surface roughness Ra, and grain size of four types of titanium sheets ((a) low glossiness and coarse grain size, (b) high glossiness and coarse grain size, (c) low glossiness and fine grain size, and (d) high glossiness and fine grain size) before dipping in the nitric-hydrofluoric acid solution

	Glossiness Gs45 (%)	Whiteness L*	Surface roughness Ra (μm)	Grain size number (GSN)
(a) Low glossiness and coarse grain size	44	70.4	2.51	6
(b) High glossiness and coarse grain size	70	67.5	1.96	6
(c) Low glossiness and fine grain size	50	71.8	2.45	9.5
(d) High glossiness and fine grain size	87	69.0	1.58	9.5

Note: Surface glossiness and roughness are adjusted by light cold rolling with dull rolls. Grain size is adjusted by controlling annealing temperature and time. All sheets are of JIS Grade 1 commercially pure titanium.

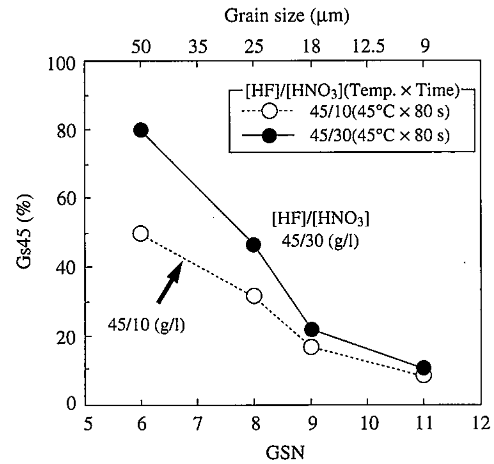


Fig. 1 Relationship between grain size number (GSN) and glossiness Gs45 of titanium after dipping in nitric-hydrofluoric acid solution

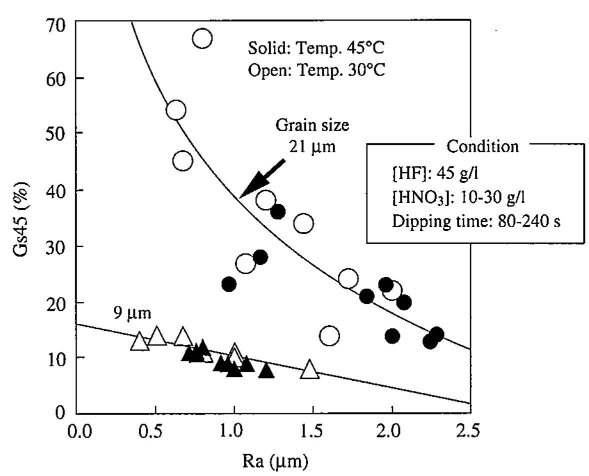


Fig. 2 Relationship between surface roughness Ra and glossiness Gs45 of titanium after dipping in nitric-hydrofluoric acid solution (when grain size is 9 and 21 μm)

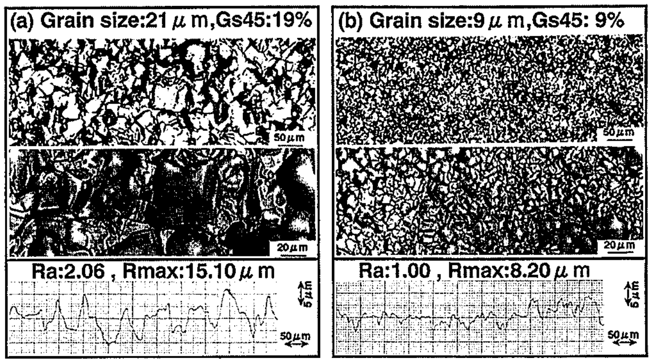


Photo 1 Surface optical micrographs and roughness profiles of titanium after dipping in nitric-hydrofluoric acid solution when grain size is 21 μm (a) and 9 μm (b) (effect of grain size)

file, the number of surface irregularities per unit length is larger. The glossiness of titanium after dipping in the nitric-hydrofluoric acid solution is thus reduced by refining the grain size, and becomes insensitive to pickling conditions like the solution composition.

3.2 Effect of initial surface condition before pickling

To compare the effect of the initial surface condition in addition to the grain size, the four types of titanium sheets listed in Table 1 ((a) low glossiness and coarse grain size, (b) high glossiness and coarse grain size, (c) low glossiness and fine grain size, and (d) high glossiness and fine grain size) were dipped in nitric-hydrofluoric acid solutions with a constant hydrofluoric acid concentration of 20 g/l and a variable nitric acid concentration of 20 to 100 g/l at 45°C. Here, the results are presented. The dissolution amount of titanium in the nitric-hydrofluoric acid solution was about 5 μm per side for a dipping time of 40 s.

The glossiness Gs45 of the four types of titanium sheets changes with dipping in the nitric-hydrofluoric acid solution as shown in **Fig. 3**. The respective types of titanium sheets change differently in the glossiness Gs45 with the nitric acid concentration. When the grain size is coarse as shown in Fig. 3(a) and (b), the glossiness Gs45 is low with the lowest nitric acid concentration of 20 g/l and high with the higher nitric acid concentration of 50 or 100 g/l. This change is a mere 10 points, however.

When the grain size is fine as shown Fig. 3(c) and (d), the glossiness Gs45 is affected by the nitric acid concentration in the nitric-hydrofluoric acid solution. When the nitric acid concentration is the lowest 20 g/l, the glossiness Gs45 drops to about 20%, regardless of its initial level. The glossiness Gs45 changes about 30 points when the initial level is a low 50% and as much as about 65 points when the initial level is a high 87%. When the nitric acid concentration is the higher 50 or 100 g/l, the glossiness Gs45 differs with the initial level. The glossiness Gs45 is 40 to 50% and changes little from the initial level when the titanium sheet is low in gloss as shown in Fig. 3(c), but drops to 55% or 70% when the titanium sheet is high in gloss as shown in Fig. 3(d).

The change in the whiteness L* of the four types of titanium sheets with the dipping time in the nitric-hydrofluoric acid solution is shown in **Fig. 4**. The whiteness L* of the four types of titanium sheets increases to 75 to 77 after a dipping time of 20 to 40 s, irrespective of the initial glossiness, whiteness as well as the grain size and the nitric acid concentration in the nitric-hydrofluoric acid solu-

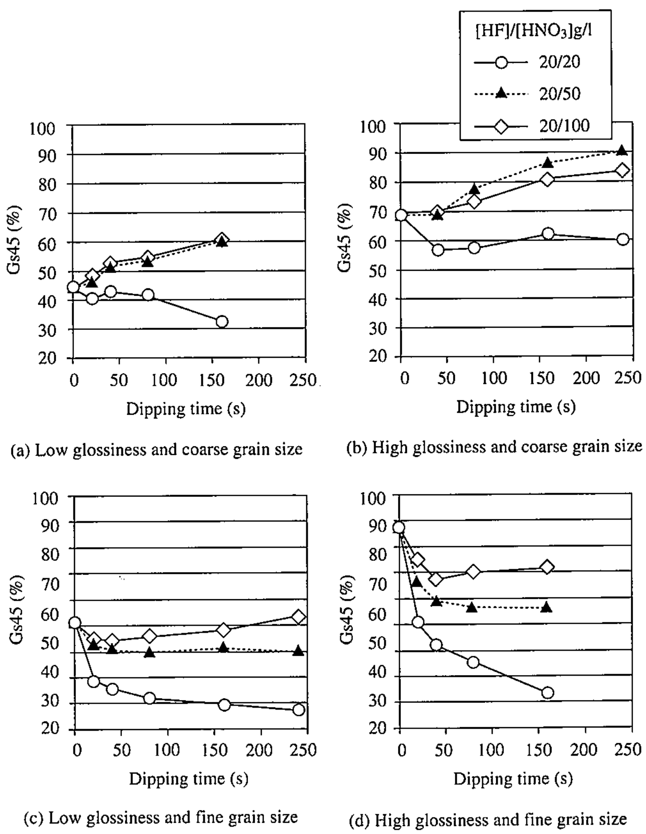


Fig. 3 Change in glossiness Gs45 of titanium sheets (four types listed in Table 1) with dipping time in nitric-hydrofluoric acid solution

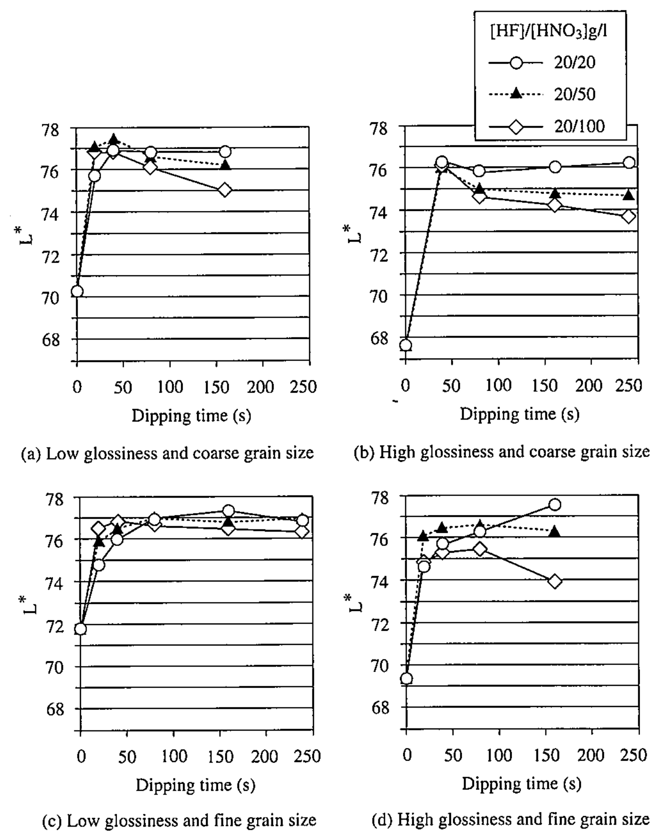


Fig. 4 Change in whiteness L* of titanium sheets (four types listed in Table 1) with dipping time in nitric-hydrofluoric acid solution

tion. When the dipping time exceeds 80 s, the whiteness L* changes little with the lowest nitric acid concentration of 20 g/l and gradually decreases by 1 to 2 points with the higher nitric acid concentration of 50 or 100 g/l.

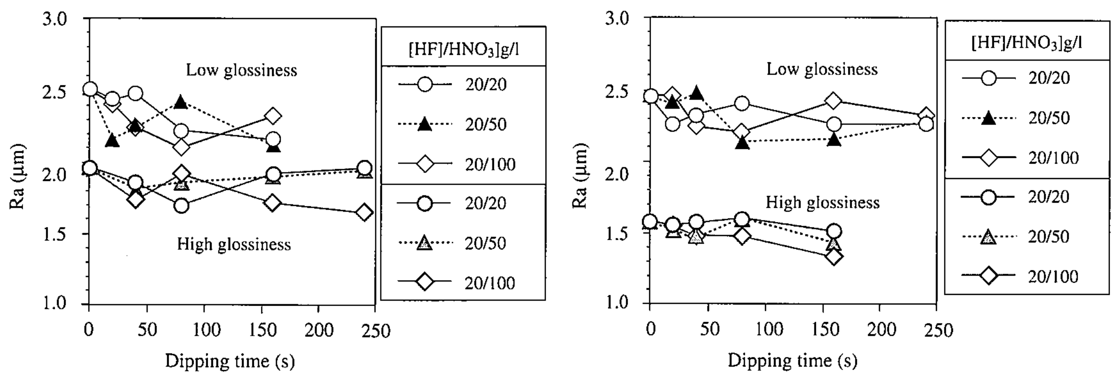
When the grain size is coarse (or the grain size number is 6), the glossiness Gs45 is affected little by the nitric acid concentration in the nitric-hydrofluoric acid solution and does not appreciably change from the initial level. When the grain size is fine (or the grain size number is 9.5), the glossiness Gs45 is greatly affected by the nitric acid concentration and markedly drops with the lowest nitric acid concentration of 20 g/l. The whiteness L* differs little with the initial surface condition and grain size, and is stable at a high level of about 74 or more for each type of titanium sheet.

4. Discussion

When the effect of the grain size alone is considered, the surface irregularities formed by pickling in the nitric-hydrofluoric acid solution are considered to arise from the anisotropy of the dissolution rate of titanium[6]. Surface irregularities of such a size as to correspond to the size of individual grains are formed. When their size is small, the individual grains are dissolved off, even with a small dissolution amount, and the surface irregularities become shallower and finer to mask the contribution of the anisotropy of the dissolution rate to their formation as shown in Fig. 1. As a result, with the surface roughness Ra being equal, a completely different surface roughness profile is obtained. As the grain size decreases, the surface irregularities become finer even when the surface roughness Ra is low. Smooth portions almost disappear as shown in Photo 1, light is diffusely reflected, and the glossiness is stabilized at a low level as shown in Fig. 1.

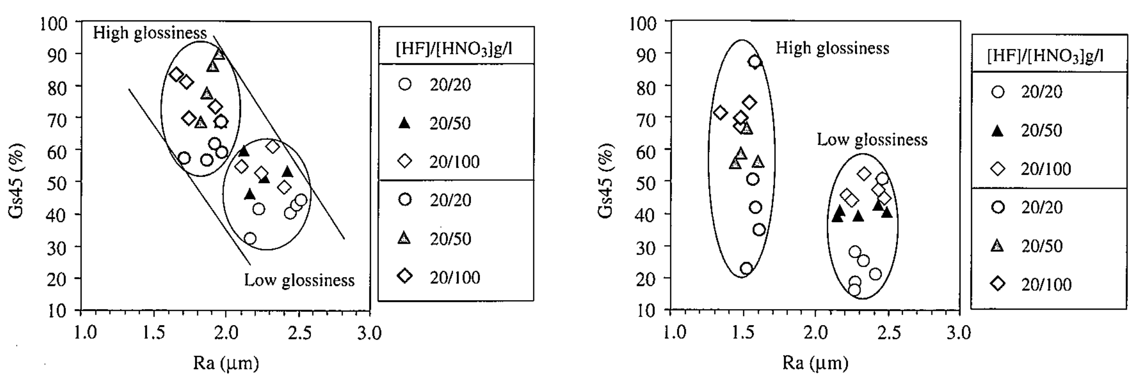
Now, the difference in the initial glossiness is considered. The glossiness after pickling in the nitric-hydrofluoric acid solution is considered to depend on both of initial irregularities formed by transfer of dull roll surface finish and irregularities formed on an individual grain basis by pickling in the nitric-hydrofluoric acid solution. The surface roughness Ra of the above-mentioned four types of titanium sheets changes little with dipping in the nitric-hydrofluoric acid solution when the surface roughness is both coarse and fine as shown in **Fig. 5**(a) and (b), respectively. The relationship between the surface roughness Ra and the glossiness Gs45 is shown in **Fig. 6**. When the grain size is coarse as shown in Fig. 6(a), the glossiness Gs45 decreases within a band with increasing surface roughness Ra. When the grain size is fine as shown in Fig. 6(b), the glossiness Gs45 is dispersed over a wide range even for the same surface roughness Ra and is found not to correlate with the surface roughness Ra.

The surface roughness profile does not appreciably change from the initial surface condition after dipping in the nitric-hydrofluoric acid solution when the grain size is coarse. If it is fine, the surface roughness profile is expected to change to a different morphology, depending on the solution composition (nitric acid concentration). For microscopic surface morphology comparison, surface optical micrographs and roughness profiles are shown in **Photo 2**(a) and (b) and **Photo 3**(c) and (d). Dipping in the nitric-hydrofluoric acid solution forms surface irregularities on an individual grain basis. When



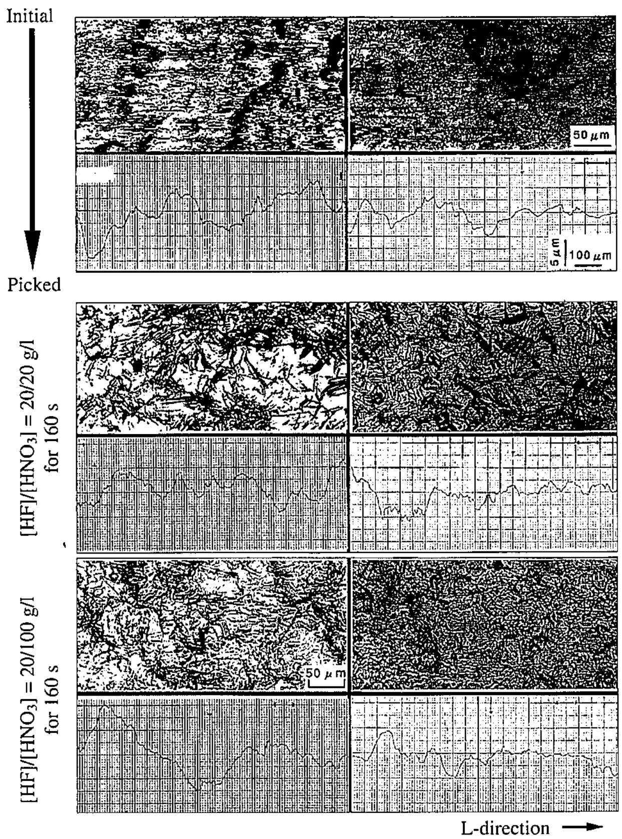
(a) Coarse grain size (b) Fine grain size

Fig. 5 Change in surface roughness Ra of titanium sheets with dipping time in nitric-hydrofluoric acid solution



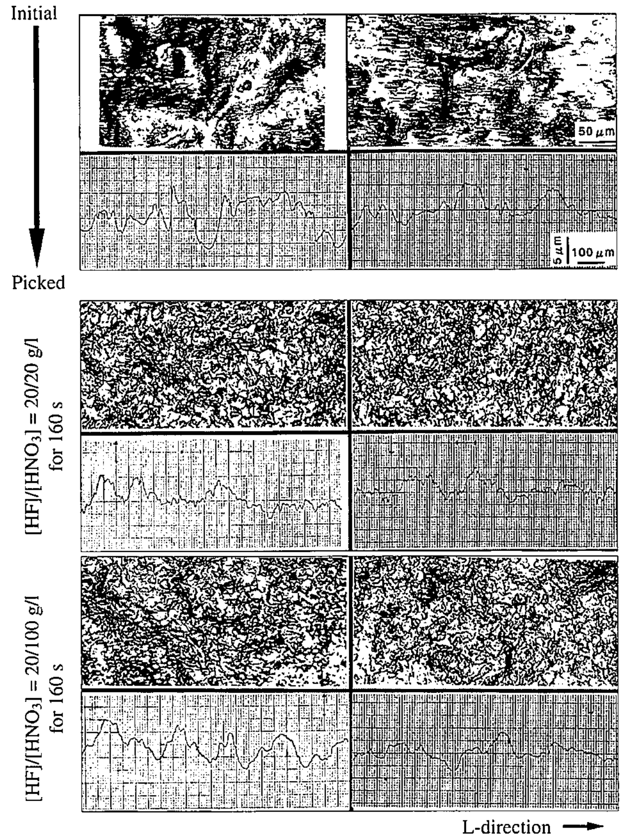
(a) Coarse grain size (b) Fine grain size

Fig. 6 Relationship between surface roughness Ra and glossiness Gs45 of titanium sheets after dipping in nitric-hydrofluoric acid solution



(a) Low glossiness and coarse grain size (b) High glossiness and coarse grain size

Photo 2 Change in surface morphology (optical micrographs and roughness profiles) of titanium sheets ((a) low glossiness and coarse grain size and (b) high glossiness and coarse grain size in Table 1) with dipping in nitric-hydrofluoric acid solution



(c) Low glossiness and fine grain size (d) High glossiness and fine grain size

Photo 3 Change in surface morphology (optical micrographs and roughness profiles) of titanium sheets ((c) low glossiness and fine grain size and (d) high glossiness and fine grain size in Table 1) with dipping in nitric-hydrofluoric acid solution

the grain size is coarse as shown in Photo 2(a) and (b), the surface irregularities formed by dipping in the nitric-hydrofluoric acid solution are as coarse as the grains and are of the same pitch as that of initial coarse surface irregularities, so that they affect the glossiness little. The glossiness (coarseness) of titanium after dipping in the nitric-hydrofluoric acid solution is considered not to change appreciably from the initial glossiness (coarse irregularities formed by transfer of dull roll finish) as shown in Fig. 3(a) and (b).

The surface irregularities are very fine, as shown in Photo 3(c) and (d), when grain size is fine. The surface roughness profiles indicate that fine-pitched irregularities are distributed on the initial coarse irregularities. (This tendency is pronounced especially when the nitric acid concentration is the lowest 20 g/l.) Consequently, the fine irregularities formed on an individual grain basis by dipping in the nitric-hydrofluoric acid solution exert a more predominant effect on the glossiness of the titanium sheets than the initial coarse irregularities, when the grain size is fine, and those irregularities are considered to produce the phenomenon of the glossiness markedly declining as shown in Fig. 3(c) and (d).

Lastly, another index, or whiteness, is discussed. Extremely fine irregularities are formed by a relatively short dipping time. These irregularities are shallow and affect little the glossiness of titanium, but are enough to scatter visible rays. The whiteness of titanium is considered to suddenly increase as a result. Removal by nitric-hydrofluoric acid pickling of the rolling oil deposited onto the titanium sheet surface by cold rolling with dull rolls is presumably another cause for the increase in the whiteness of the titanium sheets. When the nitric acid concentration is high at 50 or 100 g/l, the effect[6] of the solution composition appears with the progress of pickling. As the surface becomes gradually smother, the whiteness is presumed to decrease gradually as well.

5. Conclusions

The effects of the grain size and initial surface condition on the surface morphology of JIS Grade 1 commercially pure titanium after dipping in the nitric-hydrofluoric acid solution were studied, centering on glossiness and whiteness as indexes of antiglare quality. The following conclusions were reached.

(1) When the initial surface is finished to #600, the glossiness Gs45 after dipping in the nitric-hydrofluoric acid solution decreases with decreasing grain size or increasing grain size number. As the grain size number exceeds 9, the difference in the glossiness Gs45 with the nitric acid concentration in the nitric-hydrofluoric acid solution almost disappears.

(2) Dipping in the nitric-hydrofluoric acid solution forms irregularities on an individual grain basis on the surface of titanium. As the grain size decreases, the irregularities become shallower and finer to reduce smooth portions on the surface of titanium. As a result,

the surface of titanium diffusely reflects light and diminishes in glossiness. Since the irregularities are considered to arise from the anisotropy of the dissolution rate of titanium, individual grains are dissolved off with a small dissolution amount when the grain size is fine. Consequently, the contribution of anisotropy to the formation of irregularities on the surface of titanium is considered to become less pronounced.

(3) The effect of the initial surface condition (low and high glossiness) on the glossiness of titanium after nitric-hydro-fluoric acid pickling varies with the grain size. As grain sizes become coarse, the glossiness of pickled titanium is affected little by the initial surface condition. Since the irregularities formed by pickling on an individual grain basis are of approximately the same size as the initial surface irregularities, the glossiness Gs45 of pickled titanium changes by only about 10 points from the initial level. With fine grain sizes, the irregularities formed by pickling on an individual grain basis are finer than the initial coarse irregularities, and govern the glossiness of pickled titanium.

(4) The whiteness of pickled titanium is not affected by the initial surface condition. A short time of dipping in the nitric-hydrofluoric acid solution sharply increases the whiteness L* to more than 74. This is because shallow and fine irregularities formed by slight pickling are enough to scatter visible rays.

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