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Development of Oxidation Protective Coating for Titanium

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Abstract:

Nippon Steel developed an oxidation protective coating for titanium. When applied to titanium, the oxidation protective coating forms a titanium aluminide layer with high oxidation resistance on the titanium surface during ordinary combustion gas heating. While conventional glass-based oxidation protective coatings are not sufficiently effective, the new oxidation protective coating can effectively prevent the formation of an oxygen-hardened layer or the alpha case which is peculiar to titanium. Application of the new oxidation protective coating in the ingot breakdown process can prevent the loss of titanium and the formation of rolled-in scale from oxidation, and can simplify the grinding process to remove the alpha case.

1. Introduction

Japan's titanium industry has grown about fivefold to annual production of about 8,000 tons in the past 20 years, boosted mainly by application to such industrial equipment as electrodes and condensers. To further expand the demand for titanium, full-fledged entry must be made into the fields of construction materials and consumer goods. Needless to say, a key to success in this challenge is technological capability to produce titanium at low cost. Nippon Steel has been exploring the low-cost production of titanium in very possible aspect. Defect removal accounts for a large percentage of the titanium production cost. Defects are caused by coarse grain size of ingots, segregation, insufficient hot workability, galling on rolls, scratches, and entrapment of foreign matters, among other factors. Defects arising from oxidation that is peculiar to titanium cannot be prevented by any means on the production floor. The oxidation of titanium is characteristic in that, in addition to the scale (titanium oxide) formation, it makes oxygen diffuse and dissolve in the bulk of titanium to form a hardened layer commonly referred to as the alpha case. Unlike the scale, the alpha case cannot be removed by high-pressure water descaling, does not peel off during rolling, and thus degrades the surface quality of titanium products. After hot rolling, the alpha case and surface defects must be removed by grinding all surfaces to prevent the occurrence of defects in the subsequent processes. Grinding to the extent of staying always on the safe side increases the grinding cost and yield loss. Here is reported a new oxidation protective coating developed to effectively prevent the alpha case formation in titanium.

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2. Oxidation Characteristics of Titanium

The binding energy of oxygen for titanium is as high as for aluminum and silicon, but it is only titanium that dissolves as much as over 10 wt% of oxygen. The dissolution of oxygen increases the strength of titanium and decreases its elongation and reduction of area. When oxygen is dissolved in excess of about 0.8 wt%, titanium no longer can elongate.

Photo 1 shows a cross-sectional microstructure near the surface of commercially pure titanium when oxidized in air at 900°C for 16 h. The outermost rutile (TiO_2) scale is apt to peel in layers and is not seen in the microstructure shown. The underlying alpha case where oxygen is dissolved is as thick as about 300 μm. In the alpha case near the surface, oxygen, being an alpha stabilizer, is grown to coarse grains about 150 μm in size without any transformed structure. Substances looking like precipitates are observed inside the coarse grains. **Fig. 1** shows the increase with time in the weight of titanium due to oxidation. At 800°C, the weight gain of titanium increases generally in proportion to the

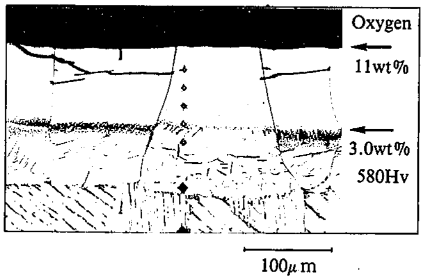


Photo 1 Cross-sectional microstructure of alpha case

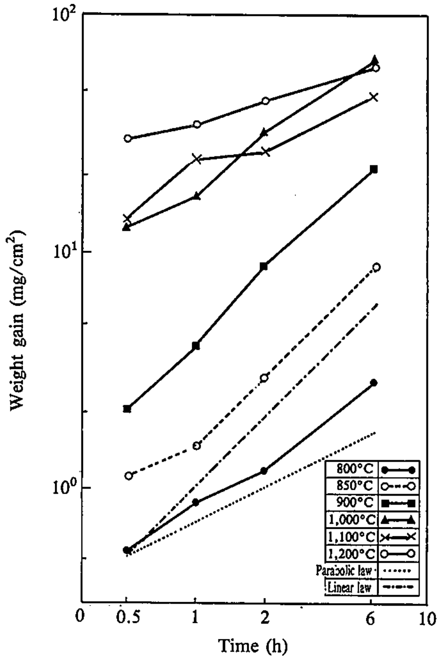


Fig. 1 Weight gain of titanium due to high-temperature oxidation

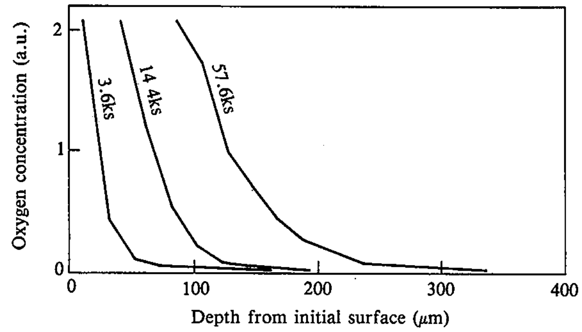


Fig. 2 Diffusion of oxygen into titanium due to high-temperature oxidation (when heated in air at 900°C)

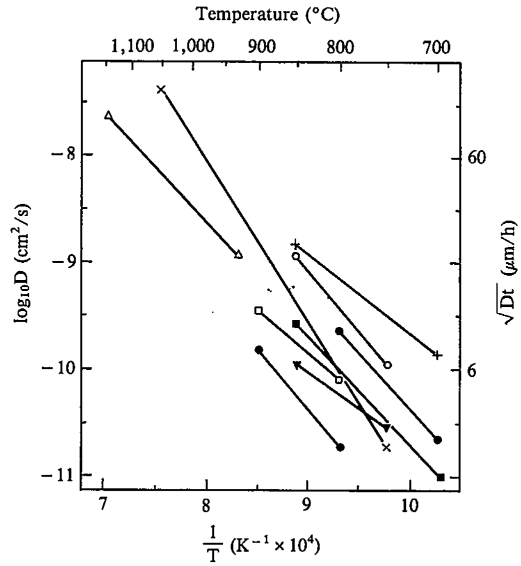


Fig. 3 Diffusion coefficient of oxygen in titanium[3)]

one-second power of time (parabolic law), and the scale is protective. When the weight gain exceeds a few milligrams per cm^2 at 850, 900, and 1,000°C, it increases approximately in proportion to the first power of time (linear law), and the scale is not protective. At 1,100°C, the weight gain increases generally in proportion to the one-second power of time, and the scale again becomes protective. The scale is tightly sintered, and the outward diffusion of titanium predominates according to the results of marker experiment[1)]. In the low-temperature region, the weight gain of titanium is known to increase in proportion to the one-third power of time at 400 and 500°C and to the one-second power of time at 700°C[2)]. The growth behavior of the alpha case with the dissolution of oxygen is as shown in **Fig. 2**. **Fig. 3** shows the diffusion coefficient of oxygen in titanium[3)]. The oxygen moves in the titanium about 20 μm in 1 h at 900°C. As shown in **Table 1**, the amount of oxygen dissolution accounts for about 10 to 20% of the weight gain of titanium due to oxidation. **Fig. 4** shows the weight gain of titanium due to the oxygen dissolution. The weight gain of titanium due to the oxygen dissolution is controlled by diffusion and is close to that indicated by the parabolic law. As shown in **Table 2**, the metal loss (thickness loss) of titanium due to scale is smaller than for iron. In the case of titanium, however, the thick alpha case formed by oxygen that accounts

Table 1 Amount of oxygen dissolution in titanium

Time (h)	1	4	16
Amount of oxygen dissolution (mg/cm^2)	0.86	1.65	2.66
Total weight gain (mg/cm^2)	3.67	13.6	26.4
Dissolution ratio (%)	22	12	10.1

JIS Class 2 commercially pure titanium, heated in air at 900°C

for a mere 10 to 20% of its weight gain must be removed by grinding. The net metal loss of titanium due to oxidation thus turns out to be about the same as for iron.

3. Oxidation Preventive Technology

Oxidation can be prevented by alloying, atmosphere heating, surface treatment, and other techniques. Study was made on the feasibility of applying these techniques to titanium.

(1) Conventionally known methods involve alloying the base metal with a suitable element, changing the chemical composition of scale and controlling the movement of diffusion species, or forming highly protective scale by selective oxidation or tightening the scale adhesion. The former method is based on the presence of scale that is protective or exhibits the parabolic law. Around the heating temperature of 1,000°C before breakdown rolling, the rutile scale has no oxidation protec-

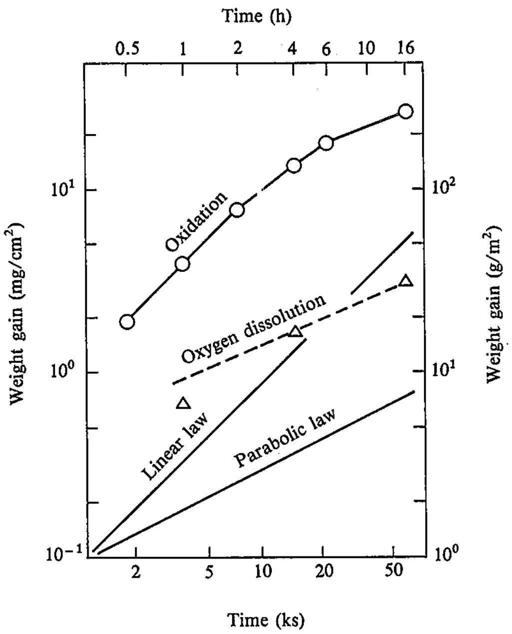


Fig. 4 Weight gain of titanium due to oxidation and weight gain of titanium due to oxygen dissolution (JIS Class 2 commercially pure titanium, heated in air at 900°C)

Table 2 Comparison of titanium and iron in thickness loss due to high-temperature oxidation

	Oxidation weight gain (mg/cm²)	Thickness loss (μm)	Alpha case (μm)	Total loss (μm)
Titanium	4	13	100	113
Iron	30	133	0	133

Heated in air at 900°C for 1 h

tion, and no large improvement can be expected. The latter method calls for an element that is much more selectively oxidizable than titanium, but no such element is available[4].

(2) The alpha case steeply declines in thickness as conventional combustion gas heating is replaced by induction heating in a nitrogen atmosphere. This is because nitrogen is slow to diffuse through a titanium nitride layer and through titanium, as compared with oxygen. Needless to say, an argon atmosphere is desirable. Unless the partial pressure of oxygen is effectively lowered, however, the alpha case formation cannot be fully inhibited.

(3) In recent years, surface treating technology has made remarkable progress so that any desired coatings can be applied to any desired substrates. For example, platinum ion plating is reported to fully protect titanium against oxidation at 650°C. When an MCrAlY alloy with excellent oxidation resistance is sprayed or vapor deposited onto titanium, there occur such problems as the growth of eutectic compounds with titanium and formation of an interdiffusion layer at the heating temperatures encountered in the titanium fabrication process, making it necessary to provide an intermediate layer of tantalum or niobium[5]. When an oxide-based coating is applied, titanium robs the oxide of oxygen. Formation of a layer that can effectively shut out oxygen is a key to solving this problem.

(4) Conventional oxidation protective coatings have been developed for iron and steel. They are easy to apply and low in cost. They are composed mainly of borosilicate glass that strongly binds with oxygen but is low in softening point, and they are very effective on iron. When the borosilicate glass-based coating is applied to titanium, it can prevent the formation of scale, but the borosilicate glass serves as a source of oxygen for titanium, and it does not serve the purpose of preventing the alpha case formation. Examples of oxidation protective coatings applied to titanium are shown in **Photo 2** and **Fig. 5**.

As discussed above, oxidation protective coatings are cost-effective and easy to apply.

4. Properties Required of Oxidation Protective Coatings

Oxidation protective coatings are required to have the following properties:

(1) Low cost: If the oxidation protective coating is more expensive than the cost of removing defects, there is no reason for its development.

(2) Field applicability: The oxidation protective coating should be easy to apply to both ingots and slabs.

(3) Control of alpha case formation: The oxidation protective coating should inhibit the diffusion of oxygen into the bulk of titanium.

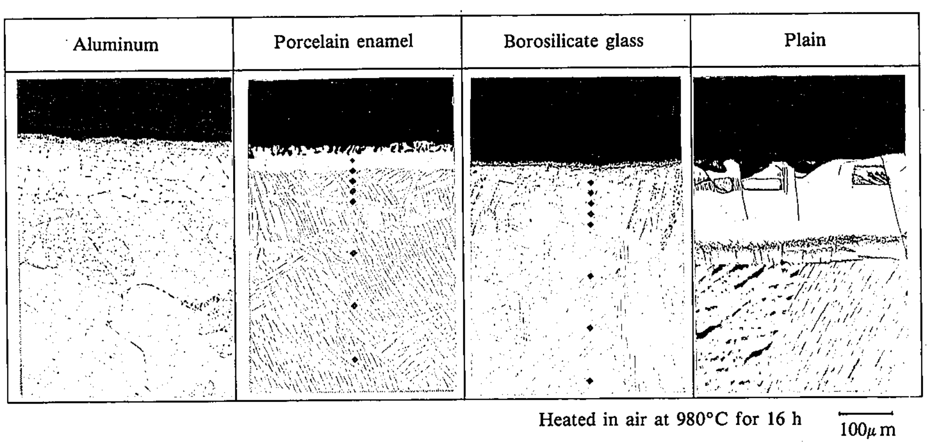


Photo 2 Cross-sectional microstructure of surface layer of titanium coated with aluminum-based or glass-based oxidation protective coating and heated

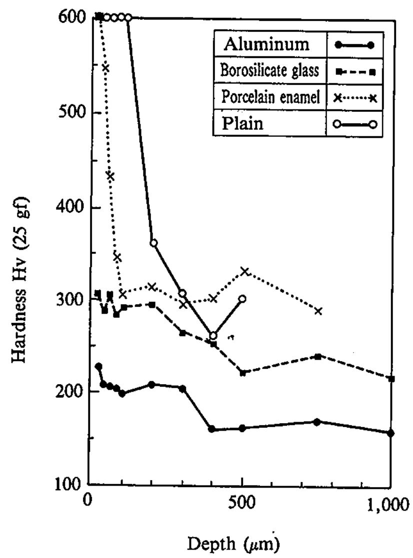


Fig. 5 Cross-sectional hardness distribution of surface layer of titanium coated with aluminum-based or glass-based oxidation protective coating and heated

(4) Harmlessness during rolling: The oxidation protective coating should not damage rolls or eat into titanium.
(5) Ease of removal: The oxidation protective coating should be easily removable by shot blasting or the like.
(6) Total reliability: The oxidation protective coating may partly peel off when grabbed by a machine or rubbed against support fixtures in the furnace, but should be capable of protecting the entire titanium surface in some way or another, including the partial grinding of oxidized portions when the oxidized portions are clearly distinguishable from the protected portion.

Some of the glass-based oxidation protective coatings cannot meet property requirements (3), (4) and (6), whereas the new oxidation protective coating satisfies all the above property requirements.

5. Development of Aluminum-Based Oxidation Protective Coating

Table 3 gives the composition of the new oxidation protective coating developed for titanium. **Photo 3** and **Fig. 6** show its effectiveness established through severe laboratory testing. Applying this oxidation protective coating prevents about 400 μm of scale loss and about 4 mm of the alpha case.

(1) The main ingredient is flaky metallic aluminum powder. Aluminum was selected because titanium was found to react with aluminum to form $TiAl_3$ that has excellent oxidation resistance during heating in air. The binder is detrimental to the prevention of oxidation and is therefore held at minimum. The flaky aluminum powder can maintain sufficient coating adhesion.
(2) An alkyd resin was selected for the binder because when used in a limited amount, it slowly decomposes and vaporizes on heating. It is important that the binder is added in a minimum amount necessary to fix the aluminum powder on the

Table 3 Composition of aluminum-based oxidation protective coating for titanium

Composition	Part by weight	Detail
Aluminum	100	Flaky, coated with stearic acid
Binder	15–40	Alkyd resin, containing metal naphthenate
Viscosity modifier	About 150	Toluene for thick coating film and xylene for thin coating film

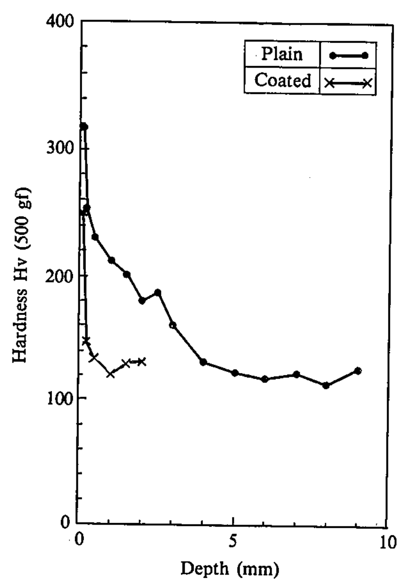


Fig. 6 Prevention of alpha case by applying aluminum-based oxidation protective coating

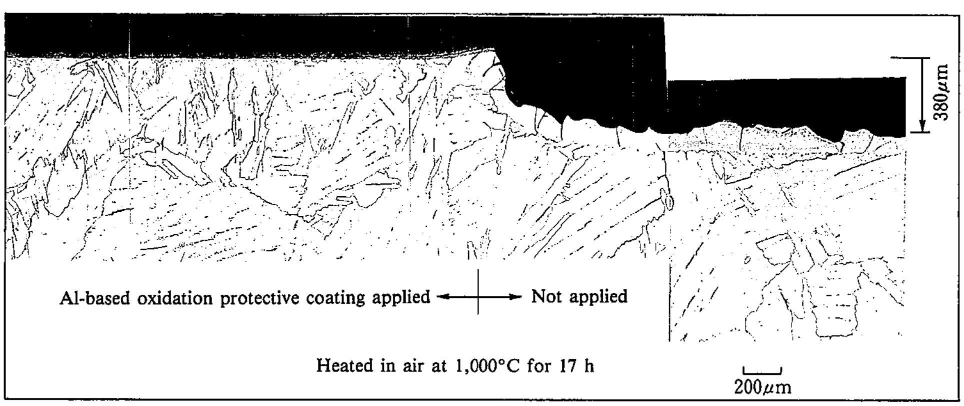


Photo 3 Effectiveness of aluminum-based oxidation protective coating

titanium surface.

(3) A viscosity modifier is required to improve the applicability of the oxidation protective coating. Rapid drying toluene is used for high-temperature service in which a thick coating film is required, while xylene is used when a thin coating film suffices.

(4) The oxidation protective coating is applied by an airless gun. Because of its composition, the oxidation protective coating is too low in viscosity to be applied by a brush and therefore must be sprayed. When it is applied to a thick film by an air spray gun, bubbles form in the film. In such a case, an airless gun should be used.

6. Oxidation Protective Mechanism

The mechanism whereby titanium is protected against oxidation by the aluminum-based oxidation protective coating is explained according to the process of application and heating in air while referring to **Photo 4** and **Fig. 7**.

(1) The alkyd resin starts to decompose at 400°C. The aluminum flakes remain on the titanium in the laminated condition.

(2) Even above the aluminum melting point of 660°C, no molten aluminum layer forms, and the aluminum flakes remain in the laminated condition, as evident from **Photo 4**.

(3) At 700 to 900°C, titanium actively reacts with aluminum. Aluminum is actively oxidized, too, but as can be seen from **Fig. 7**, metallic aluminum amply remains in the powder up to 800°C.

(4) At 1,000°C, aluminum is completely oxidized into alumina.

The microscopic reaction process between titanium and aluminum is presumed to follow the course shown in **Fig. 8**. That is,

(i) A thin alumina film forms on the aluminum powder surface, and the metallic aluminum in the bulk remains up to high temperatures.

(ii) Titanium ions diffuse through the thin alumina film and form $TiAl_3$ in the bulk of the aluminum powder. This reaction is exothermic and proceeds at an explosive rate.

(iii) When the coating thickness is thin, the initially formed $TiAl_3$ undergoes interdiffusion between titanium and aluminum and gradually changes to TiAl or Ti_3Al with the lapse of time at temperatures of 1,000°C and above, resulting in deteriorating the oxidation resistance.

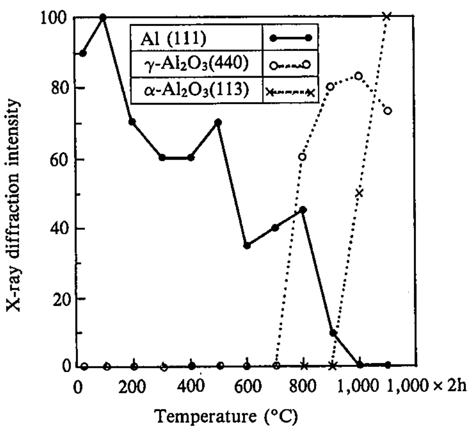


Fig. 7 Oxidation of aluminum in aluminum-based oxidation protective coating during heating

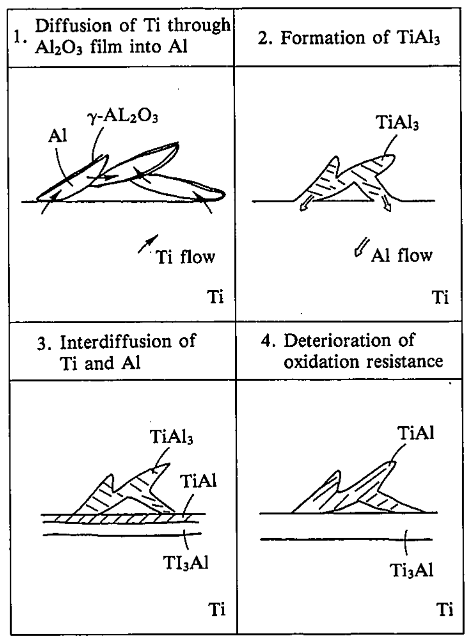


Fig. 8 Estimated progress of reaction between aluminum-based oxidation protective coating and titanium

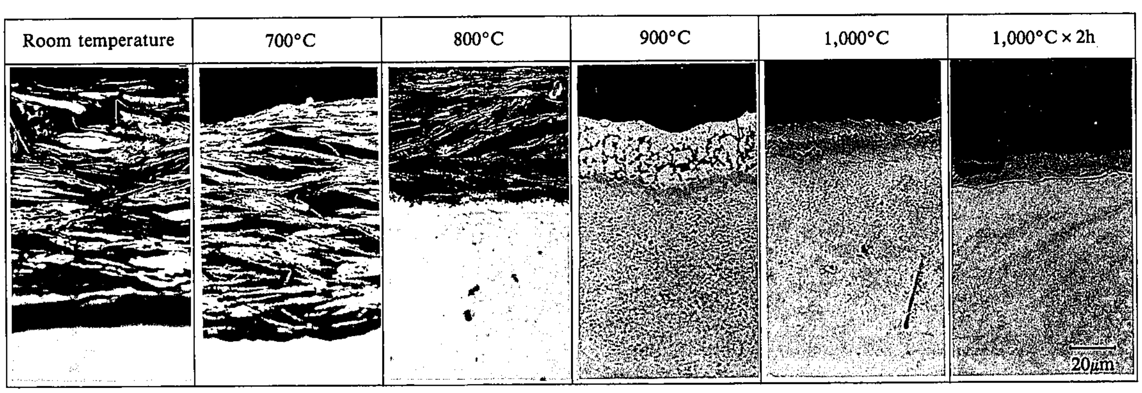


Photo 4 Formation of oxidation resistant film by aluminum-based oxidation protective coating during heating

7. Production Line Application Test

The new aluminum-based oxidation protective coating was applied on the breakdown rolling process. The oxidation protective coating was applied to one half of an ingot, as shown in **Photo 5**. Slab conditioning was changed from total grinding to a combination of shot blasting and partial grinding, and the resultant yield improvement and finishing cost reduction were surveyed.

(1) Surface appearance of breakdown: As shown in **Photo 6**, the coated surface is free from rolled-in rutile scale and is smooth. When the oxidation protected portion is rolled, grayish white streaks are produced at right angles to the rolling direction, making it possible to distinguish from the oxidized portion.

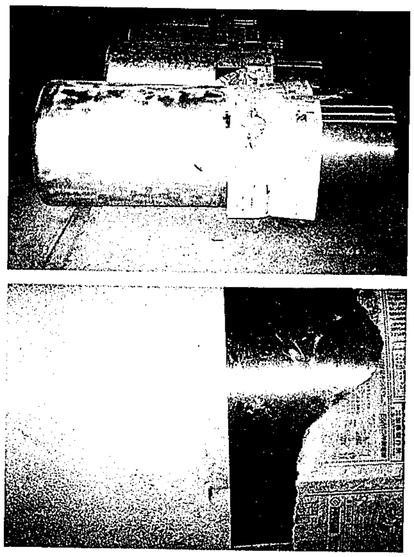


Photo 5 Titanium ingot with aluminum-based oxidation protective coating

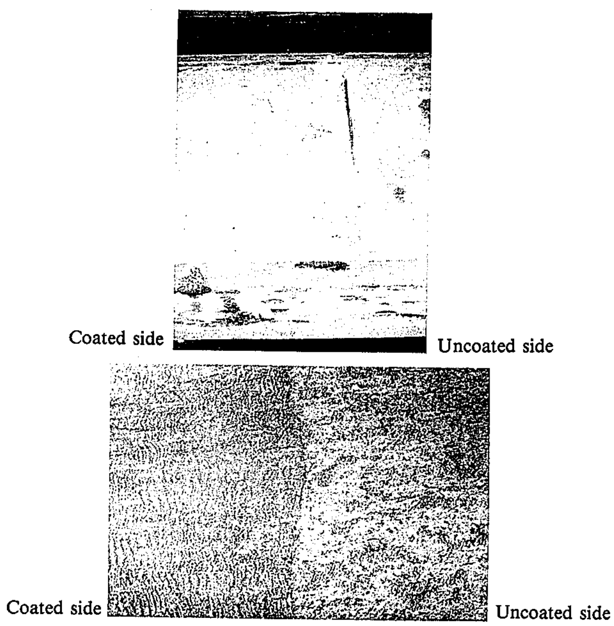


Photo 6 Change in surface texture of breakdown with application of aluminum-based oxidation protective coating

(2) Protection against oxidation: **Photo 7** shows the cross-sectional microstructure of a slab to which the oxidation protective coating was applied. No alpha case is formed, which demonstrates the effectiveness of the oxidation protective coating. As can be seen from **Fig. 9**, the absence of a thick alpha case makes it unnecessary to grind the slab.

(3) Surface appearance of slab: The surface of the breakdown that was reheated, rolled into a slab, and shot blasted is shown in **Photo 8**. The coated portion clearly has better surface quality. Since the reheating temperature was relatively low, the breakdown was reheated without reapplying the oxidation protective coating.

(4) When the slab was rolled into a plate, the plate was found to have no surface quality problems.

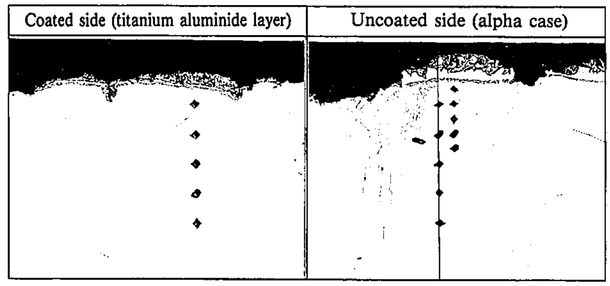


Photo 7 Change in surface structure of breakdown with application of aluminum-based oxidation protective coating

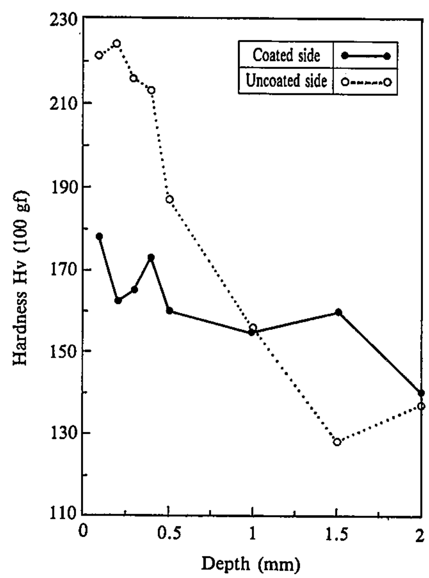
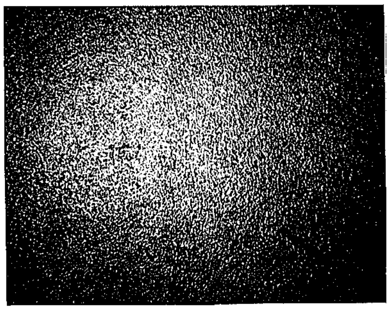
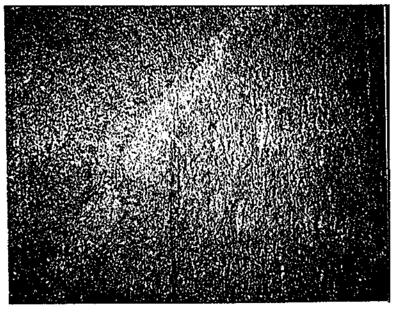


Fig. 9 Change in surface hardness of breakdown with application of aluminum-based oxidation protective coating



Coated side



Uncoated side

Photo 8 Change in surface texture of slab with application of aluminum-based oxidation protective coating

8. Conclusions

(1) A new aluminum-based oxidation protective coating was developed to omit or simplify the removal of defects from titanium.

(2) Field tests proved that the oxidation protective coating is greatly effective in protecting titanium against oxidation and reducing the occurrence of defects in titanium, and thus in simplifying the defect removal.

(3) The oxidation protective coating is now in the process of application on a production basis, expansion of the range of applicable processes, and application to alloys.

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