Technical Report

Development of High Corrosion-Resistant Titanium Material with Reduced PGM Content

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Abstract

The effects of PGMs on titanium corrosion resistance were studied. As a result, initial corrosion resistance was deteriorated by a reduction in the amount of PGMs. However, the corrosion-resistant deterioration dissolved by adding a trace amount of another element, for example yttrium. Furthermore, the depassivation pH was remarkably improved by the addition, even though the PGM content of the titanium material was reduced. Based on these findings, high corrosion-resistant titanium material was developed. Advantages of the titanium material are high corrosion resistance, cost-effectiveness, and environmentally-friendly (lower GWP and TMR). The chemical composition of the titanium material is sustainable. The performance of its high corrosion resistance will contribute to the long lifespan of electrolyzers which produce clean hydrogen. Therefore, high corrosion-resistant titanium material is effective for reducing CO_2 emission and material requirements indirectly.

1. Introduction

Titanium forms a passivation film on the surface as a protective layer and shows excellent corrosion resistance, and is used for seawater equipment and/or for chemical industry applications. However, in a high-temperature and high-concentration chloride environment, it may be crevice corroded. In a non-oxidizing acid environment, it may be generally corroded. Therefore, high corrosion-resistant titanium material superior to that of commercially pure titanium is required.

Against this background, several high corrosion-resistant titanium materials were developed in the past. In 1959, Stern and Wissenberg revealed that high corrosion-resistant materials were significantly improved by adding 0.064–0.60% of one of the platinum group metals (PGMs) of Pt, Pd, Rh, Ru, Ir, and Os to titanium.[1] The addition of PGMs having a low hydrogen overpotential promotes the cathode reaction, and hence, the material potential is ennobled. By the potential ennoblement, the passivation of titanium is promoted, and the depassivation pH, which is described later, is lowered and the corrosion resistance is improved. As a result, the crevice corrosion resistance and the general corrosion resistance in a non-oxidizing acid environment are improved.[2, 3] Based on this finding, ASTM-Gr.7 (Pd: 0.12–0.25%) is widely used as a high corrosion-resistant titanium material. Griess discovered the corrosion resistance improving effect not only of Pd, but also of Mo and Ni in 1968.[3] Later in 1982, Tomashov et al. conducted a study to improve the corrosion resistance with the compound addition of Ni and Mo to titanium, and the titanium is used as ASTM-Gr.12 (Ni: 0.60–0.90%, Mo: 0.20–0.40%).[4] Although ASTM-Gr.12 does not contain PGMs, there are cases in which its application is limited because it is inferior in corrosion resistance to the PGM-added titanium materials such as ASTM-Gr.7.[5–10] The development of the high corrosion-resistant titanium materials announced after ASTM-Gr.12 is premised on them containing PGMs. Their development history is explained using the following examples: after 1985, Taki et al. conducted a study to improve corrosion resistance by the compound addition of Ni and Ru, which was standardized and is used as ASTM-Gr.13 (Ni: 0.4–0.6%, Ru: 0.04–0.06%). In 1991, Kitayama and Shida conducted a study where even the addition of Pd to titanium by 0.05% exhibits corrosion resistance equivalent to that of ASTM-Gr.7, which was standardized, and is used as ASTM-Gr.17 (Pd: 0.04–0.08%). Since 1994, Ueda et al. and Yashiki et al. conducted research to improve the corrosion resistance by the compound addi-

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tion of Ni, Pd, Ru, and Cr to titanium, which was standardized and is used as ASTM-Gr.33, Gr.34 (Ni: 0.35–0.55%, Pd: 0.01–0.02%, Ru: 0.02–0.04%, Cr: 0.10–0.20%).[11–19] The above is the history of the development of the high corrosion-resistant titanium materials in the past. However, these developments did not take "sustainability" into account. In recent years society has become more strongly "sustainable" due to concern about the destruction of the global environment. Thus, the following issues have arisen with the high corrosion-resistant titanium materials.

2. High Corrosion-resistant Titanium Material Alloy Element and Sustainability

Of the two social issues, the first is that the alloying elements to be added are rare elements and expensive. **Figure 1** shows the price trend of PGMs which summarizes the price figures published by the United States Geological Survey (USGS), and derives the annual average price of PGMs as \$/g.[20–22] The price trend is explained with the focus on Pd added to many high corrosion-resistant titanium materials. In 1959, the annual average price of Pd was lower than that of Pt. From then until 1999, the annual average price of Pd continued to remain lower in relation to Pt. However, between 1977 and 1980, the annual average price of Pd soared to 6.4 \$/g, which was about four times higher, and remained at the level until 1996 with some fluctuations. Between 1996 and 2000, the annual average price of Pd soared, about five times as high as 22.2 \$/g. The rise in the annual average price of Pd is correlated with the development period of the high corrosion-resistant titanium materials, and it can be seen that the development was highly motivated by the raw material price and economic efficiency. The annual average price of Pd in 2019 was 49.5 \$/g and the average price of Pd in 2020 was 67.5 \$/g. The annual average price of Pd is 80–110 times higher than the price in 1959 when Stern and Wissenberg published a study on adding PGMs to titanium to improve corrosion resistance. In recent years, the annual average price of PGMs has tended to soar further. High corrosion-resistant titanium materials, which are premised on the addition of PGMs, are problematic due to the soaring raw material price and their stability.

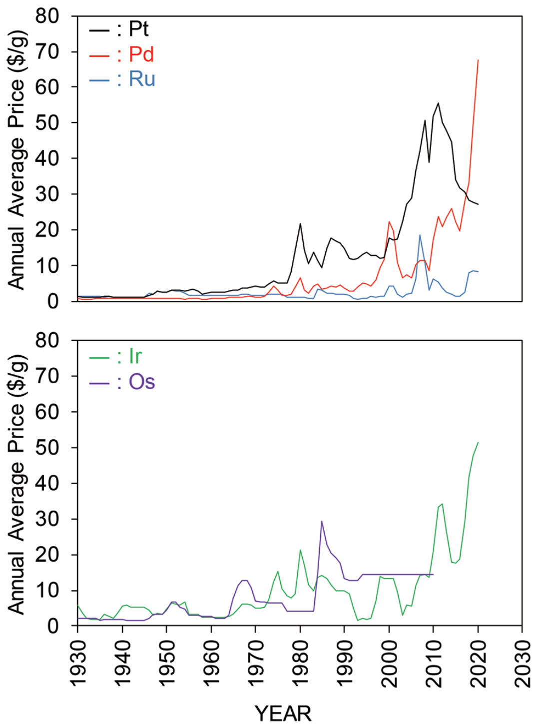

Fig. 1 Annual average price transition of PGMs[20–22]

The second issue is that the addition of PGMs to high corrosion-resistant titanium materials is not suitable for the projects that take sustainability into account because industrial uses of PGMs have a large environmental load. The situation is further explained in some of the literature in the environmental field.[23–25] The indicators for considering the environmental load of materials include the Global Warming Potential (GWP) from the viewpoint of emissions, and the total material requirement (TMR) from the viewpoint of resource consumption. The GWP in this report considers the weight of the greenhouse gases emitted when producing 1 kg of each element. The TMR is an index that evaluates the hidden material flow as well as the direct and indirect material input. The hidden material flow means, for example, the transfer of rocks, earth, and sand associated with mining, deforestation, the change of the water system inclusive of its water required for oil-well drilling, and the flow of materials required for the land regeneration and landscape protection. The selection of the alloying element that enables the best performance with the lowest possible amount in terms of both GWP and TMR is considered when developing an environmentally-friendly and sustainable material.

Figure 2 cites and shows the relationship between GWP and TMR of various elements.[25] Ti, the base material, is relatively low with respect to both GMP and TMR, and the industrial scrap titanium can be reused by using an electron beam melting furnace, and is recognized as an environmentally-friendly material. On the other hand, regarding the additive elements, except for Ru, the PGMs explained in the previous section have extremely high GWP and TMR. Since the low GWP and TMR are desirable from the viewpoint of sustainability, even though the amount of PGMs added is small, the high corrosion-resistant titanium materials developed in the past are not necessarily environmentally-friendly, and are problematic from the perspective of sustainability.

In order to solve these two issues, Nippon Steel Corporation is currently promoting the R&D of high corrosion-resistant titanium materials with reduced PGM content.

3. Development of High Corrosion-resistant Titanium

3.1 Effect of reduction of PGM content on corrosion resistance of titanium

Firstly, the effect of the reduction of Pd in the cases of the conventional ASTM-Gr.17 and ASTM-Gr.7 is explained. For evaluation of the corrosion resistance, two indicators of depassivation pH and the potential ennoblement time were used. **Figure 3** shows a measurement example of depassivation pH. The depassivation pH is one of the indicators for the corrosion resistance of titanium and/or stainless steel, and denotes the boundary condition of pH at which point the passivation film fails to be formed as a protective layer. The lower this value, the higher the density of an acid where the passivation film can be formed, and the greater the excellence in corrosion resistance. Furthermore, the same applies to the crevice corrosion that occurs under a local acidic environment; the lower the depassivation pH, the higher the resistance to the crevice corrosion. In the example of Fig. 3, a pH of about 0 becomes the boundary condition, and with a pH higher than 0, the material is passivated. The dark reddish-brown color of the photo shows the interference color developed by the mature passivation film, the circumfer-

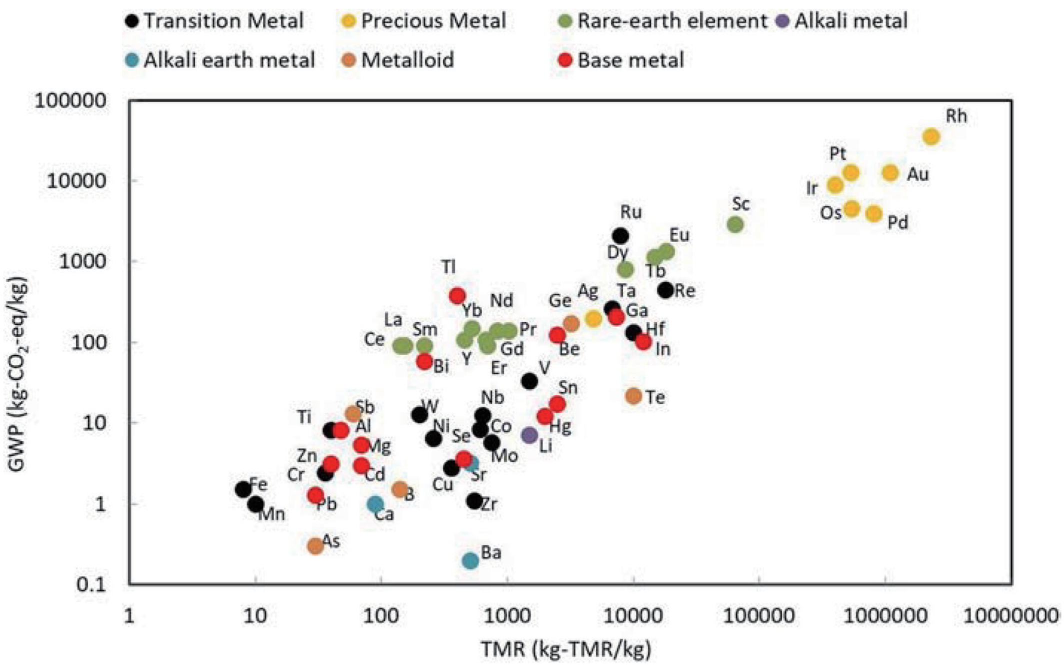

Fig. 2　Relations between GWP and TMR[25]

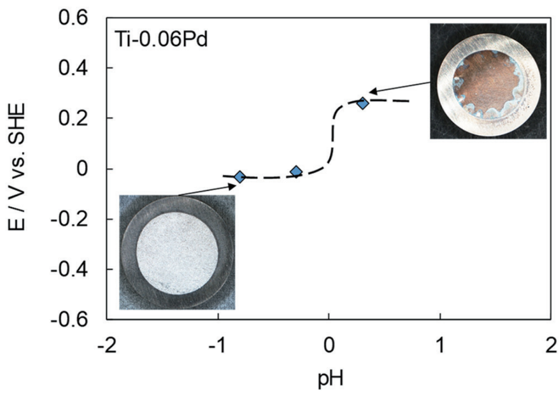

Fig. 3　Measurement example of depassivation pH in deaerated acid solution at 90°C

ence of which had been protected from exposure to the acid solution by packing material during measurement, and the metallic luster of that before the test remained. With a pH lower than 0, the thinning of the metal due to corrosion had progressed clearly enough to be visually recognizable.

The potential ennoblement time is the time required for the establishment of the potential noble after it is immersed in the test solution; the shorter it is, the earlier the passivation is established, and the higher the corrosion resistance in the initial immersion stage becomes. In this report, in the case of pH = +0.3, the potential on which the potential ennoblement time is based was set at −0.2 V vs. SHE. The immersion potential behavior of several titanium materials having different content of added Pd is reported.[26] With the common behavior being independent from the amount of Pd addition, in the initial stage of immersion, the potential drops to about from −0.5 to −0.4 V vs. SHE. Later, the immersion potential is ennobled about from −0.1 to +0.1 V vs. SHE. Furthermore, the immersion potential is ennobled gradually with the immersion time and passivation is established, and the immersion potential stabilizes. As for the potential independent from the amount of Pd added in the potential ennoblement behavior, this time, −0.2 V vs. SHE was set as the standard for the potential ennoblement time. This potential standard approximately corresponds to the midpoint of the respective passivating potential of the passivation films formed by the rutil type TiO_2 and $TiO_2 \cdot H_2O$. Either test was conducted in a deaerated acid solution at 90°C wherein the pH was adjusted by adding HCl water solution to the 250 g/L NaCl water solution, and the test continued until the immersion potential stabilized.

Figure 4 shows the effect of the Pd addition amount on the depassivation pH, and **Fig. 5** shows the effect of the Pd addition amount on the titanium ennoblement time. The depassivation pH is about 0 independent from the Pd addition amount. On the other hand, the potential ennoblement time becomes longer as the Pd addition amount becomes smaller. ASTM-Gr.1 does not reach −0.2 V vs. SHE, and therefore, is not passivated. From these results, in the case that the Pd addition amount is decreased, although the depassivation pH as the boundary condition is not adversely affected, the potential ennoblement time becomes longer, and in the early stage of immersion, the titanium dissolution time is also extended, and the corrosion resistance in the early stage of immersion deteriorates.

3.2 Effect of trace addition of third element on corrosion resistance of PGM-added titanium

As explained in the previous section, if the amount of Pd added is reduced to 0.02%, the potential ennoblement time becomes longer, and the corrosion resistance in the initial stage of immersion deteriorates. This deterioration of corrosion resistance can be solved by adding a trace amount of a third element like yttrium (Y). **Figure 6** shows the effect of the addition amount of Y on the depassivation pH of Ti-0.02Pd, and **Fig. 7** shows the effect of the addition amount of Y on the potential ennoblement time of Ti-0.02Pd. The addition of 0.01–0.02% Y lowers the depassivation pH to about −0.8, greatly improving the corrosion resistance. The potential ennoblement time is also shortened, and the problem that the dissolution time of titanium becomes longer in the initial stage of immersion can be solved.

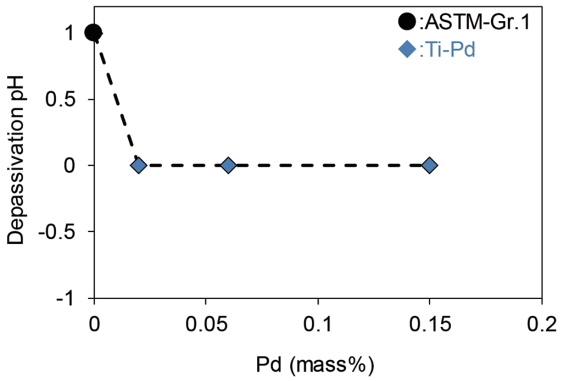

Fig. 4 Effect of Pd addition amount on titanium depassivation pH in deaerated acid solution at 90°C

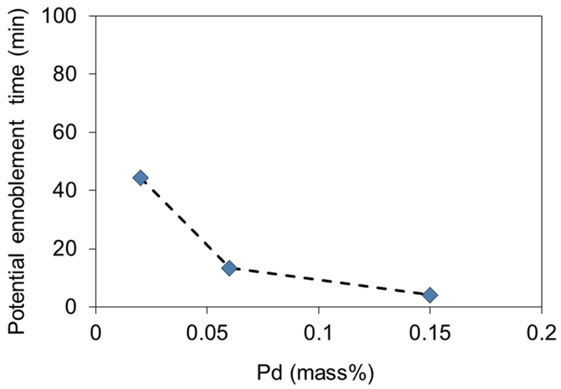

Fig. 5 Effect of Pd addition amount on titanium potential ennoblement time in deaerated acid solution (pH=+0.3) at 90°C

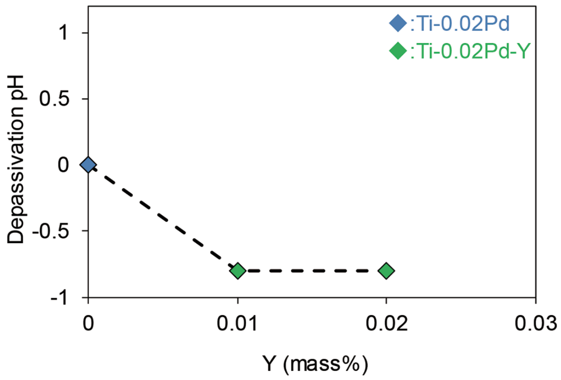

Fig. 6 Effect of Y addition amount on Ti-0.02Pd depassivation pH in deaerated acid solution at 90°C

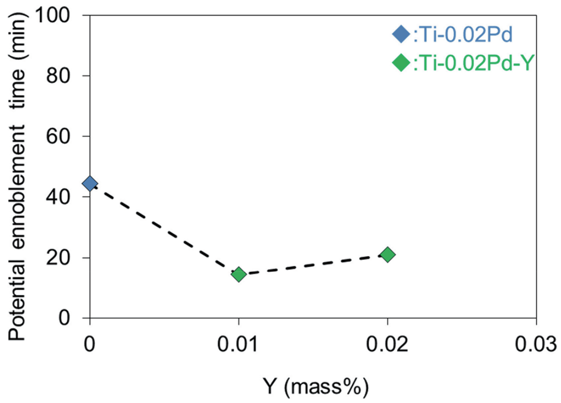

Fig. 7 Effect of Y addition amount on Ti-0.02Pd potential ennoblement time in deaerated acid solution (pH=+0.3) at 90°C

Next the mechanism of improving the corrosion resistance with the addition of a trace amount of the third element is explained. The co-existence of ions containing Y in the solution in the initial stage of immersion has the effect of promoting the passivation of titanium. The third element to be added in a trace amount is not limited to Y alone, but misch metal (Mm) and the like have the same effect. The PGMs to be added are not limited to Pd only, and the same corrosion resistance is exhibited even when Ru with a lower TMR is added. The mechanical properties of the developed material are equivalent to that of ASTM-Gr.1, and are also excellent in workability and formability.

Based on the above findings, we have developed a titanium material that achieved balance between the reduction of the amount of PGM addition and high corrosion resistance.

4. Comparison of GWP and TMR of High Corrosion-resistant Titanium

For the purpose of comparing and evaluating the sustainability of the developed high corrosion-resistant titanium materials, GWP and TMR of high corrosion-resistant titanium materials are shown in **Fig. 8** and in **Fig. 9**, respectively. These graphs have been created by estimating the GWP and TMR of the respective element from Fig. 2, and by calculating according to the weight ratio of the addition amount of the respective element to titanium material. The effects of Fe and/or oxygen that slightly exist in the titanium materials conventionally have been excluded. Ti-0.15Pd and Ti-0.06Pd are used as the representative chemical compositions of ASTM-Gr.7 and ASTM-Gr.17, respectively. As for Mm, the contents have been assumed as 50% for each of La and Ce, and the mix proportion as 0.01%. GWP and TMR of the high corrosion-resistant titanium material developed this time are lower than those of the conventional high corrosion-resistant titanium materials. Lowering of TMR is particularly remarkable, and it is the material that is the most environmentally friendly from the viewpoint of reducing the resource consumption.

5. Expected Usage

Use of the developed titanium material is expected in the chemical industry wherein the high corrosion resistance is required, and is particularly beneficial in the application to electrolyzers for producing hydrogen. **Table 1** shows the corrosive environments and the products of electrolyzers.[27–29)]

5.1 Chlor-Alkali electrolyzer

The chlor-alkali electrolyzer produces Cl_2 and NaOH as the main products by electrolysis of the high concentration sodium chloride solution. Since the anode side of the electrolyzer is exposed to the high sodium chloride concentration solution at high temperature, high corrosion resistance is required. Conventionally, for the crevice structure material that requires particularly high corrosion resistance for the anode side, ASTM-Gr.7 and/or ASTM-Gr.17 were used. However, influenced by the soaring Pd price in recent years, the cost of the raw materials remains a problem.

In addition, the chlor-alkali electrolyzer is used not only for the production of chemical products, but also has the function of producing hydrogen as a byproduct. Conventionally, the byproduct hy-

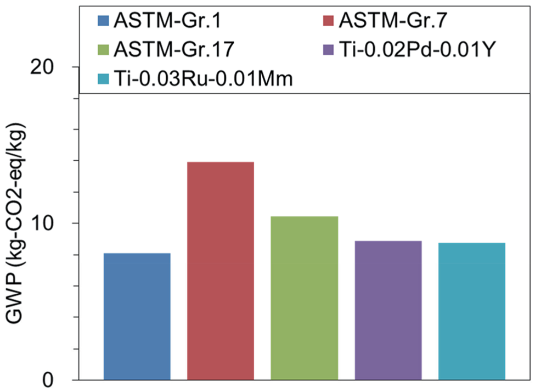

Fig. 8 GWP of high corrosion-resistant titanium materials

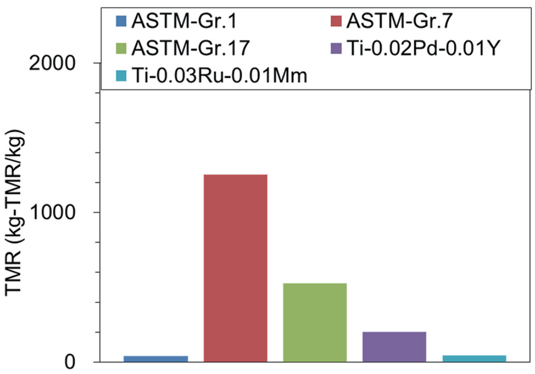

Fig. 9 TMR of high corrosion-resistant titanium materials

Table 1 Environments and products of electrolyzers[27–29)]

	Environments		Products
	Anode	Cathode	
Chlorine-Alkaline electrolyzer	NaCl solution	NaOH solution	NaOH Cl_2 H_2
PEM water electrolyzer	Acid solution		H_2, O_2

drogen produced by the chlor-alkali electrolyzer has not been effectively utilized. However, due to the orientation toward decarbonization in recent years, the byproduct hydrogen will be utilized in a more effective manner. By using the developed high corrosion-resistant titanium material, the predominance in the raw material price, and the longer than expected lifespan, the low GWP and TMR are realized for use as the component materials of the electrolyzer.

5.2 PEM (Proton Exchange Membrane) water electrolyzer

The water electrolyzer produces hydrogen by water splitting, and is expected to be beneficial for producing green hydrogen using renewable energy as a power source. Since it is necessary to cope with the long-time operation in an acidic environment, the component material is required to have high corrosion resistance. In many cases, Pt and Ir are used for the catalyst layer in a water electrolyzer, and they are not always sustainable materials from the viewpoint of GWP and TMR. By further reducing the PGMs in the catalyst layer, it is possible to produce hydrogen that is environmentally-friendly in terms of constituent materials. From the viewpoint of corrosion resistance, the use of the developed high corrosion-resistant titanium material is expected to provide a longer lifespan than that of conventional materials.

6. Conclusion

To solve the issues of raw material price and sustainability, we investigated the effect of reducing the amount of PGM addition on the corrosion resistance of high corrosion-resistant titanium materials, and developed a high corrosion-resistant titanium material that realizes low GWP and TMR. The following findings were obtained.

(1) When the amount of Pd to be added to titanium is reduced, the depassivation pH, is not adversely affected; however, the potential ennoblement time is prolonged, and therefore, the corrosion resistance in the initial immersion stage is deteriorated.

(2) Even in the case of the reduction of the amount of Pd addition to titanium materials, the corrosion resistance is improved by the addition of a third element like Y, the potential ennoblement time is the same as that of ASTM Gr.17 (Ti-0.06Pd), and excellent depassivation pH exceeding that of ASTM Gr.7 (Ti-0.15Pd) is exhibited.

(3) As compared with the conventional high corrosion-resistant titanium materials, the developed high corrosion-resistant titanium material has low TMR in particular, and contributes to sustainability.

The developed high corrosion-resistant titanium material contributes not only to the sustainability of the elements to be added, but also to the long lifespan of the chlor-alkali electrolyzer and/or the water electrolyzer that produce hydrogen. With its application to hydrogen production, its contribution to the sustainability of all society is expected.

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