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Characteristics of High-Corrosion Resistant Titanium Alloy TICOREX and Its Applications


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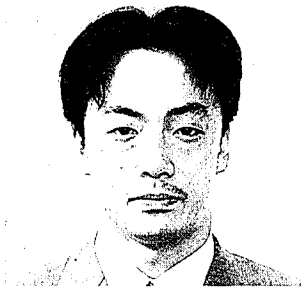
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Abstract

Commercially pure titanium (C.P.Ti) has excellent corrosion resistance. However, crevice corrosion and general corrosion may take place on C.P.Ti in NaCl solutions and in non-oxidizing acid solutions. Ti-0.15Pd is applied in such serious environments, although it is very expensive, because noble palladium is added. Ti-0.5%Ni-0.05%Ru (TICOREX) was developed which provides competitive low cost and excellent corrosion resistance as same as Ti-0.15%Pd. By analyzing corrosion-resistant mechanism of TICOREX , it is clear that Ti_2Ni including much ruthenium enhances potential of TICOREX to passivation region by means of decreasing in hydrogen over-voltage. TICOREX was standardized in American Society for Testing and Materials (ASTM) and has already been applied in many plants.

1. Introduction

Commercially pure titanium is a metal with excellent corrosion resistance. For example, it suffers little or no general corrosion, pitting corrosion, or stress corrosion cracking in acid solutions or seawater in which stainless steel and copper alloys are easily corroded[1]. For this reason, commercially pure titanium is used in various chemical plants and heat exchangers that use seawater. Accompanying the

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increasing severity of corrosive environments in recent years, however, even commercially pure titanium corrodes, in some cases. In a high-temperature solution containing chlorine ions, titanium develops crevice corrosion if it has fine crevices. In aqueous solutions of non-oxidizing acids (e.g., HCl and H_2SO_4), titanium has general corrosion if the pH of the solution is low.

Under the above-mentioned corrosive environments, the Ti-0.15%Pd alloy with higher corrosion resistance than commercially pure titanium is sometimes used. Use of expensive palladium as an alloying element makes the price of the Ti-0.15Pd alloy more than double that of commercially pure titanium, and therefore poses an economical problem for the Ti-0.15Pd alloy. The authors developed and commercialized a low-cost titanium alloy (tradenamed TICOREX) with corrosion resistance approximately equivalent to Ti-0.15%Pd alloys by adding 0.05% ruthenium and 0.5% nickel to titanium[2,3]. Ruthenium is a platinum group metal like palladium, lowers the hydrogen over-voltage, and concentrates in Ti_2Ni to enhance its effectiveness. The properties and application examples of the new titanium alloy TICOREX are described below[4].

2. Properties of TICOREX

2.1 Effects of ruthenium and nickel on corrosion resistance[5]

Fig. 1 shows a typical microstructure of TICOREX. Equiaxed grains with a size of about 20 μm are observed. At the same time, fine precipitates are observed at the grain boundaries and within the grains. Such precipitates are not observed in commercially pure titanium. When TICOREX is examined by X-ray diffraction, alpha titanium diffraction peaks are observed like in commercially pure titanium. At the same time, a peak not found in alpha titanium is seen at $2\theta = 41.3°$. This agrees with the diffraction peaks of the (511) and (333) planes of Ti_2Ni. In other words, Ti_2Ni, which is not observed in commercially pure titanium, is precipitated in alpha titanium in TICOREX.

To confirm the morphology in which ruthenium is present, specimens were buffed, and portions containing precipitates were analyzed by electron probe microanalysis (EPMA) for quantitative mapping of ruthenium and nickel. **Fig. 2** shows a composition image of a measured region. The portions that appear white are precipitates recognized in Fig. 1, and the other portions are the matrix. EPMA quantitative maps of nickel and ruthenium are shown in **Figs. 3 and 4**, respectively. The nickel concentration distribution is very uneven, and nickel is not detected in the titanium matrix. The positions where nickel are present clearly correspond to the positions of the precipitates shown in Fig. 2, and the nickel concentration is 20% or more. Ruthenium is partly detected in the matrix as well, and is strongly

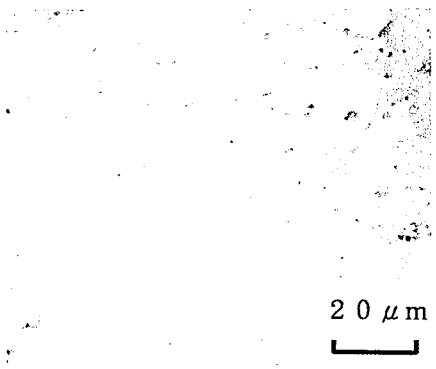

Fig. 1 Microstructure of Ti-0.5%Ni-0.05%Ru alloy

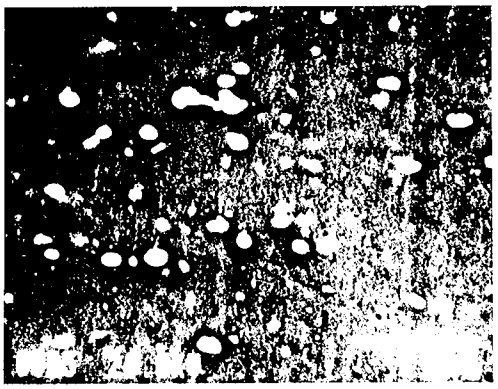

Fig. 2 Composition image of Ti-0.5%Ni-0.05%Ru alloy (many white grains are observed)

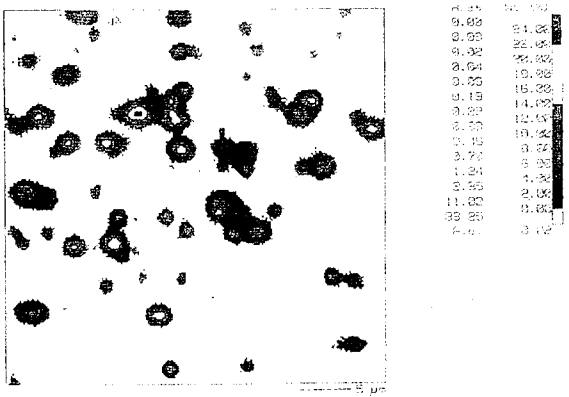

Fig. 3 EPMA quantitative map of element nickel in Ti-0.5%Ni-0.05%Ru alloy

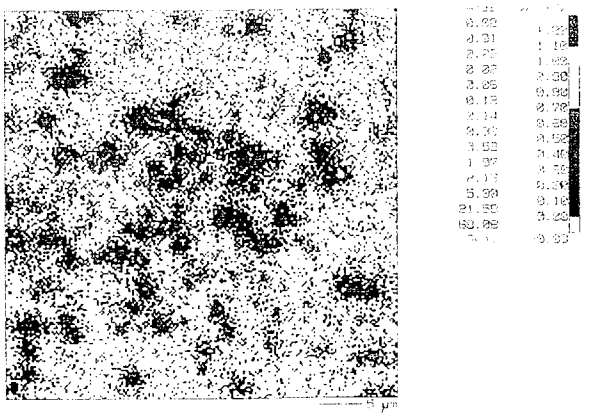

Fig. 4 EPMA quantitative map of element ruthenium in Ti-0.5%Ni-0.05%Ru alloy

detected in the positions similar to those of nickel or where the precipitates are present.

The maximum ruthenium concentration is about 1.2% and is more than 20 times higher than the initial ruthenium addition of 0.05%. In this way, ruthenium is almost all-present in Ti_2Ni precipitated (Ti_2Ni where ruthenium is concentrated is hereinafter abbreviated to as Ti_2Ni-Ru). The test results concerning the effect of this Ti_2Ni-Ru on corrosion resistance are described below.

To obtain the Ti_2Ni intermetallic compound and ruthenium-con-

taining Ti_2Ni or Ti_2Ni-Ru, titanium was mixed with nickel and ruthenium and was arc melted. The ingot obtained was homogenization annealed at 750°C for 72 h and furnace cooled, and was used to prepare three types of specimens. The chemical compositions of these specimens are given in **Table 1**. The No. 1 specimen is Ti_2Ni, and the Nos. 2 and 3 specimens are Ti_2Ni-Ru. Specimens numbered 1 to 3 were embedded in a resin so that the area ratio of the specimen material to titanium became 1:100. Each electrode produced in this way and a commercially pure titanium sheet were immersed in a 5%HCl, 80°C solution, and the potential of the commercially pure titanium sheet was measured. Commercially pure titanium is actively dissolved in this environment and exhibits a low potential. At 200 s after the immersion, Ti_2Ni or Ti_2Ni-Ru was electrically connected to the commercially pure titanium sheet. As shown in **Fig. 5**, the potential of the commercially pure titanium sheet immediately rose to more than –0.2 V and entered the passive region. The potential rise of the titanium after the electrical connection was higher for the No. 2 or 3 specimen than for the No. 1 specimen. When the electrical connection was broken, the potential of the commercially pure titanium fell back to the corrosion potential.

Table 1 Chemical analyses (mass%) of arc-melted specimens

Specimen	Ni	Ru	Ti
No.1	36.0	—	Balance
No.2	35.6	0.68	Balance
No.3	35.1	1.66	Balance

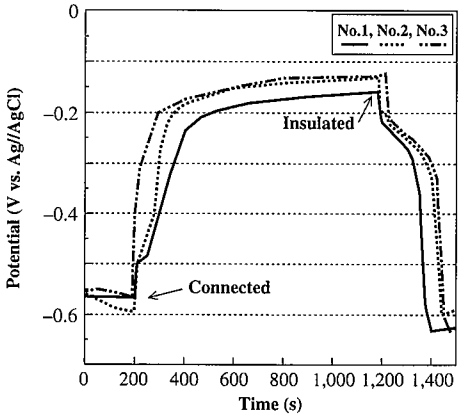

Fig. 5 Change in potential of commercially pure titanium when connected to Ti_2Ni or Ti_2Ni-Ru (area ratio: Ti:Ti_2Ni or Ti_2Ni-Ru = 100:1)

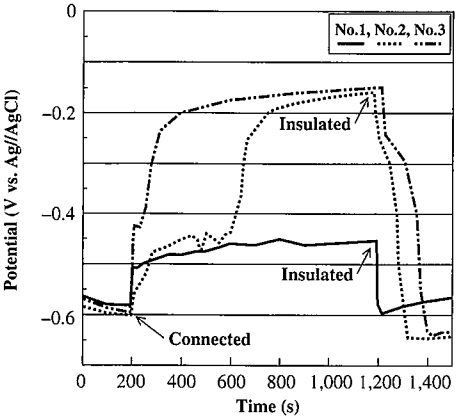

Fig. 6 Change in potential of commercially pure titanium when connected to Ti_2Ni or Ti_2Ni-Ru (area ratio: Ti:Ti_2Ni or Ti_2Ni-Ru = 250:1)

Another set of specimens was prepared by adjusting the electrode area ratio of commercially pure titanium to Ti_2Ni or Ti_2Ni-Ru to 250:1. The test results obtained when commercially pure titanium was electrically connected to these specimens are shown in **Fig. 6**. When commercially pure titanium was connected to Ti_2Ni (No. 1 specimen), the potential of commercially pure titanium slightly rose to just above about –0.5 V. When commercially pure titanium was connected to Ti_2Ni-Ru (No. 2 or No. 3 specimen), the potential of commercially pure titanium rose to the passive region. It is evident that Ti_2Ni-Ru is more capable of passivating titanium than Ti_2Ni. When titanium is brought into contact with Ti_2Ni or Ti_2Ni-Ru and the area ratio is above a certain level, it is found that the potential of titanium rises to improve the general corrosion resistance of titanium in acids like hydrochloric acid solutions.

The above results indicate that the addition of ruthenium and nickel to titanium cause the precipitation of Ti_2Ni with concentrated ruthenium or Ti_2Ni-Ru in the alpha titanium matrix and that Ti_2Ni-Ru keeps the potential of titanium electrochemically noble and improves the corrosion resistance of titanium.

2.2 General corrosion resistance of TICOREX

The isocorrosion diagrams of TICOREX and other metals in hydrochloric acid and sulfuric acid solutions are shown in **Figs. 7 and 8**, respectively. It can be seen that TICOREX has far higher general

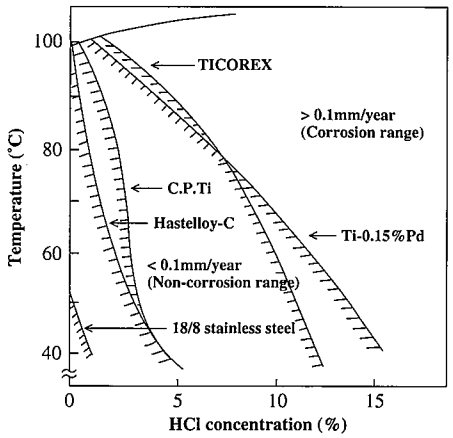

Fig. 7 Isocorrosion diagram for HCl solution

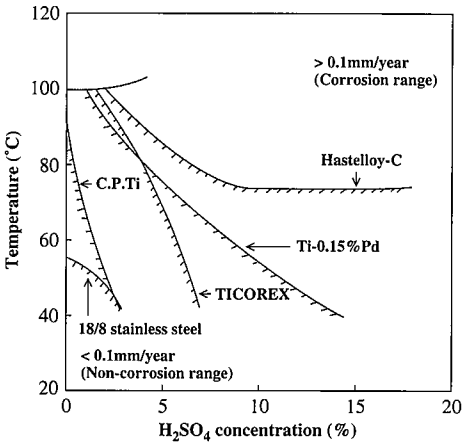

Fig. 8 Isocorrosion diagram for H_2SO_4 solution

corrosion resistance than commercially pure titanium and has approximately the same general corrosion resistance as the Ti-0.15%Pd alloy. This excellent general corrosion resistance is attributable to the uniform precipitation of Ti_2Ni-Ru in the alpha titanium matrix as noted above. TICOREX was heat treated at 600, 700, 820 or 900°C for 1 h and then rapidly quenched. The specimens thus obtained were corrosion tested. The specimens were heat treated at 600 and 700°C in the alpha region, at 820°C in the alpha-plus-beta region, and at 900°C in the beta region. The corrosion test specimens were buffed for surface examination. They were immersed in a boiling 5%HCl solution for 24 h, removed from the solution, washed in pure water, and dried. Their corroded surfaces were then observed by scanning electron microscopy (SEM). The corrosion rate of each specimen was also determined to know the effect of the corrosion rate on the microstructure.

SEM micrographs of corroded surfaces of the specimens are shown in **Fig. 9**[6]. Pits, about 2 to 3 μm in size, are observed on the corroded surface of the 600°C annealed specimen. Pits and grain boundaries are observed on the corroded surface of the 700°C annealed specimen. On the corroded surface of the 820°C annealed specimen, pits are observed within the grains, and the grain boundaries are severely corroded. The 900°C annealed specimen exhibits a corrosion morphology completely different from that of the 820°C annealed specimen, or a acicular pattern. **Fig. 10** shows the relationship between the annealing temperature and corrosion rate of TICOREX. The 600°C and 700°C annealed specimens exhibit similar corrosion rates. The corrosion rate of the 820°C annealed specimen is higher than that of the 600°C and 700°C annealed specimens. The 900°C annealed specimen is still higher in the corrosion rate and is poor in corrosion resistance. In this way, the heat treating temperature changes the precipitation condition of Ti_2Ni-Ru and hence the corrosion rate of TICOREX. It remains unchanged, however, that the heat treated specimens each have a corrosion rate far lower than that of commercially pure titanium and feature good corrosion resistance.

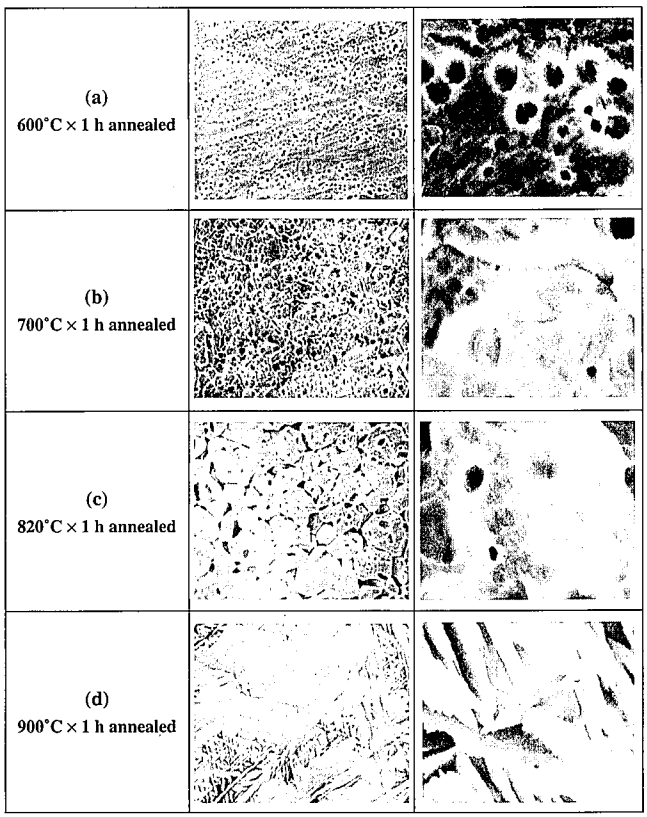

Fig. 9 Corroded surfaces of TICOREX when immersed in boiling 5% HCl solution for 24 h

2.3 Crevice corrosion resistance of TICOREX

The crevice corrosion resistance of TICOREX as evaluated by accelerated test[3] is shown in **Fig. 11**. The crevice corrosion resistance of TICOREX is superior to that of commercially pure titanium and Grade 12 (Ti-0.8%Ni-0.3%Mo) and equivalent to that of the Ti-0.15%Pd alloy. Various theories are advanced for the occurrence of crevice corrosion in titanium. Approximately, crevice corrosion arises from decrease in pH and increase in chlorine ion concentration within crevices. This environment apparently resembles the environment of general corrosion in the above-mentioned hydrochloric acid solution. Actually, titanium in the initial stage of crevice corrosion exhibits a more uniformly corroded surface than a pitted surface. In that sense, the excellent crevice corrosion resistance of TICOREX may be attributed to the electrochemical effect of the Ti_2Ni-Ru pre-

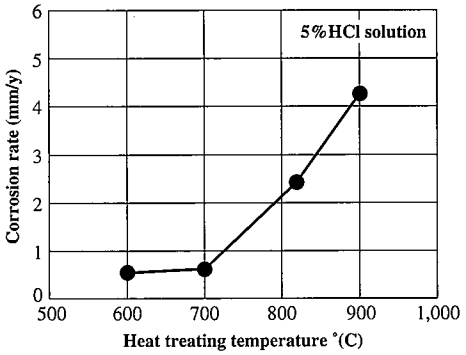

Fig. 10 Relationship between heat treating temperature and corrosion rate

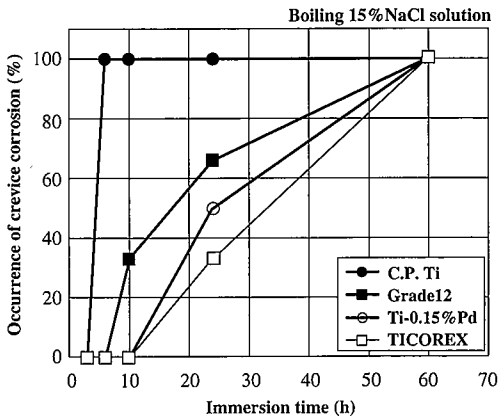

Fig. 11 Accelerated crevice corrosion test results of titanium alloys

Table 2 Grades and chemical compositions of TICOREX (JIS H 4600)

Grade	Chemical composition (%)							
	N	C	H	Fe	O	Ru	Ni	Ti
21	≤0.03	≤0.08	≤0.015	≤0.2	≤0.10	0.04 - 0.06	0.4 - 0.6	Balance
22	≤0.03	≤0.08	≤0.015	≤0.3	≤0.15	0.04 - 0.06	0.4 - 0.6	Balance
23	≤0.05	≤0.08	≤0.015	≤0.3	≤0.25	0.04 - 0.06	0.4 - 0.6	Balance

Table 3 Mechanical properties of TICOREX (sheet, plate and strip) (JIS H 4600)

Grade	Tension test				Bend test		
	Thickness (mm)	Tensile strength (N/mm^2)	Yield strength (N/mm^2)	Elongation (%)	Thickness (mm)	Bend angle	Inside radius
21	0.2 - 15	275 - 450	≥170	≥24	0.5 - 5	180°	Twice thickness
22	0.2 - 15	410 - 530	≥275	≥20	0.5 - 5	180°	Twice thickness
23	0.2 - 15	483 - 630	≥380	≥18	0.5 - 5	180°	Thrice thickness

cipitation as already noted for the case of general corrosion.

2.4 Grades and mechanical properties of TICOREX

TICOREX is classified into three grades (Grade 13, Grade 14, and Grade 15) in ASTM B 265. TICOREX is also classified into three grades (Grade 21, Grade 22, and Grade 23) in JIS H 4600 revised in February 2001 (refer to **Table 2**). The three JIS grades are the same in the nickel and ruthenium contents and corrosion resistance, but are different in the oxygen and iron contents. These different oxygen and iron contents change their mechanical properties (refer to **Table 3**). Grade 21 has the lowest oxygen and iron contents to decrease strength and increase ductility and is used in applications where workability is a critical requirement. Grade 23 has the highest oxygen and iron contents to increase strength. Grade 22 has intermediate workability and strength.

3. Application Examples of TICOREX

3.1 Soda plant[7]

A soda plant produces sodium hydroxide and chlorine gas by electrolyzing salt. Sodium hydroxide was traditionally made by an amalgamation process using mercury. Its mercury pollution problem forced the adoption of the diaphragm process in its place. The diaphragm process, however, was unable to produce sodium hydroxide of high purity and was in turn replaced by the ion exchange membrane process. TICOREX is used as material for the frames to support the ion exchange membranes. **Fig. 12** illustrates the application and operating environment of TICOREX. Since a gap is formed between the gasket and frame, commercially pure titanium develops crevice corrosion in this high-temperature high-chloride ion atmosphere. This problem led to the use of TICOREX in this application. Since a 2.5-mm thick sheet of TICOREX is formed into a square pipe, Grade 13 is used in consideration of bendability.

3.2 Salt making plant[8]

Salt is manufactured from rock salt overseas, but is mostly produced from seawater in Japan. The moisture content of seawater is removed by heating and evaporation. A heat exchanger is required for this purpose. Shell and tube heat exchangers constructed of copper alloy tubes were conventionally used. These tubes suffered general corrosion and had to be periodically replaced. As a solution, a heat exchanger made of TICOREX was fabricated for a heating pan. Given the possibility of salt depositing on the tubes and tube sheet to cause crevice corrosion between the salt and titanium, the heat exchanger was built from about 1,130 TICOREX tubes with a diameter of 42.7 mm, wall thickness of 0.7 mm and length of 7,450 mm each and from steel/TICOREX (50/4 mm) roll-clad plates.

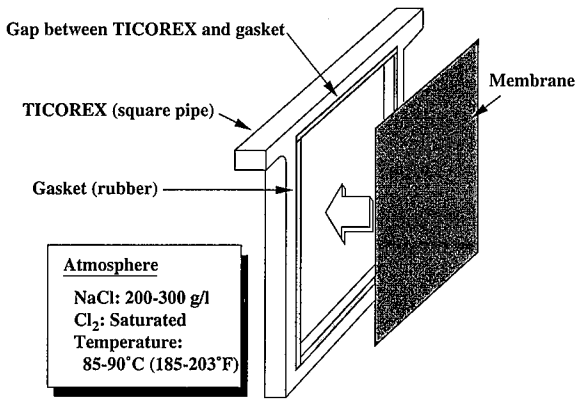

Fig. 12 Schematic illustration of TICOREX application at soda plant

3.3 Petroleum plant

TICOREX tubes (38.1 mm diameter by 0.7 mm thick by 9,052 mm long) and clad plates (4 mm thick TICOREX and 32 mm thick steel) were used in a heat exchanger of the air fin cooler type for cooling and liquefying the gas exiting the top of an atmospheric distillation column for refining crude oil.

4. Conclusions

Now that the palladium price is widely fluctuating, users are expected to more highly evaluate the excellent crevice corrosion resistance and economy of TICOREX and exploit TICOREX in more than ever applications. Nippon Steel's patents concerning TICOREX are listed in **Table 4**.

Table 4 List of patents concerning TICOREX

Registered patent	Registration date	Valid until
(1) Patent No. 1522963 Process for manufacture of titanium alloy material with excellent corrosion resistance	October 12, 1989	September 3, 2006
(2) Patent No. 1627279 Welding electrode	November 28, 1991	December 8, 2006
(3) Patent No. 1696795 Process for manufacture of titanium alloy material with excellent corrosion resistance and press formability	September 28, 1992	March 9, 2007
(4) Patent No. 1798028 Titanium alloy with excellent corrosion resistance	November 12, 1993	November 22, 2004
(5) Patent No. 1861554 Titanium alloy material with excellent corrosion resistance	August 8, 1994	November 19, 2005
(6) Patent No. 1861556 Titanium alloy material with excellent corrosion resistance	August 8, 1994	December 5, 2005
(7) Patent No. 1861558 Titanium alloy with high strength and high corrosion resistance	August 8, 1994	December 24, 2005
(8) Patent No. 2640511 Process for manufacture of titanium alloy containing ruthenium and nickel	May 2, 1997	October 14, 2008

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