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Development and Application of the New Low Alloy Steel (ARU-TEN™) Exhibiting Good Corrosion Resistance

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Abstract

We developed new corrosion resistant steel (ARU-TEN™) that exhibits good corrosion resistance closer to that of stainless steels in high chloride environments. Corrosion resistance of ARU-TEN steel is derived from a combination of inorganic zinc primer coating and the addition of Cr and Al etc. to the steel. It results in passivation of the steel surface due to a weak alkaline environment by corrosion products of the inorganic zinc primer and alloying elements added. ARU-TEN is an environment-friendly low alloy steel that minimizes the amount of rare-metal alloy addition and the application of ARU-TEN is gradually expanding for steel making plants in seashore areas. In addition, ARU-TEN shows good anti-rust resistance in mild corrosion environments such as indoor environments without the inorganic zinc primer and it is expected to be used as precision instruments in indoor environments.

1. Introduction

With the rapid economic development on a global basis in recent years, there is growing concern about the economic risk that is ascribable to the depletion or localization of producing area of rare metals such as Pt, Pd, Cr, and Ni. Under that condition, positive efforts are being made to effectively utilize the alloying elements, develop alternative technologies, etc.[1–3]

Rare metals such as Cr, Ni, Sb, and W are added to steel materials to improve the corrosion resistance of steel products. For example, stainless steels, which contain 11% or more Cr and have a passive film formed on the surface, can be used in various corrosion environments. As representative examples of low-alloy corrosion-resistant steels, weathering steels[4, 5] containing Cr, Ni, Cu, and P and used for bridges, etc., and S-TEN™[6] containing Sb, Cu, etc. and used in sulfuric acid and hydrochloric acid dew point corrosion environments, such as the flue gas treatment equipment of a thermal power station, can be cited. In a specific corrosion environment, those steels that contain only small amounts of alloying elements exhibit good corrosion resistance. However, there are no low-alloy corrosion-resistant steels that show sufficient corrosion resistance in high salt environment. In such an environment, stainless steel is mainly used.

Focusing on the combination of alloying elements and surface treatments and not just the addition of alloying elements, we launched a basic study on low alloy corrosion resistant steels based on a new concept that permits reducing the addition of Cr, Ni, and other rare metals significantly and good anti-rust resistance comparable to that of stainless steels.

Numerous studies on the sacrificial corrosion protection and the corrosion-protective effect given by a zinc-based corrosion product after corrosion of the galvanized steel plate exist.[7] It has also been reported that galvanized stainless steel exhibit good corrosion resistance due to the barrier effect of the zinc corrosion product, as well as the sacrificial corrosion protection.[8]

Therefore, we inverstigated improving the corrosion resistance of steel by combining various types of alloying elements with a zinc corrosion product. As a result, through the use of an inorganic zinc rich primer applied for the primary rust prevention of steel plates for ships, etc. and the optimization of amounts of addition of Cr and Al, we could successfully develop an economical low-alloy steel, ARU-TEN™ (Anti-RUst), which reduces the amounts of addition of rare metals to about one-fourth those of stainless steels and is comparable in ARU resistance to stainless steels. ARU-TEN is being applied to chemical plants, steelworks, etc. that are required to exhibit good

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corrosion resistance in high chloride environments.

ARU-TEN contains several percent of Cr and Al. In relatively mild corrosive environments with low chloride concentrations, such as indoors, the steel can safely be used unpainted. Therefore, it should be applicable even to the precision equipment for indoor use.

In this paper, we shall describe the corrosion resistance of ARU-TEN under various corrosion environments and the mechanism of the development of the corrosion resistance, together with the mechanical properties and typical applications of the steel.

2. Corrosion Resistance of ARU-TEN in Severe Corrosion Environment

2.1 Experimental method

An example of ARU-TEN chemical composition is shown in **Table 1**. As the reference steels, mild steel, 5%Cr steel, and Type 304 stainless steel were used. The test samples used were 60 mm (or 70 mm) in width, 150 mm in length, and 3 mm in thickness. Several test samples were unpainted (subjected to machine finishing) and other test samples were coated with inorganic zinc rich primer. Coated with inorganic zinc rich primer, test samples were subjected to steel grit blasting before it was coated with the inorganic zinc rich primer on the steel surface to an aimed thickness of 15 μm. The test sample was scribed in the bottom to simulate a coating film defect, seal-coated on the back and sides, and subjected to a corrosion test. As the corrosion test simulating an high chloride environment, cyclic corrosion test (CCT) using artificial seawater was conducted. The test conditions (per cycle) were (1) spraying of artificial seawater (35°C × 4 h), (2) drying (60°C, 10%–15%RH × 2 h), and (3) Humid (50°C, RH > 95% × 2 h). Test samples were subjected to a maximum of 150 cycles. In the CCT, which was intended for speedy evaluation of the corrosion resistance, an inorganic zinc rich primer (Zn content of heating residue: about 55%) that contains a relatively small proportion of Zn and that is used in shipbuilding, etc. was applied.

2.2 Experimental results and discussions

2.2.1 Results of evaluation of corrosion resistance

Figures 1 and **2** show the appearances of the unpainted test samples and primer-coated test samples after the corrosion test. The unpainted test sample of ARU-TEN shows general corrosion as do those of the mild steel and 5%Cr steel. In the case of the test samples coated with inorganic zinc rich primer, red rust is observed on the entire surface of the mild steel and near the scribed part of the 5%Cr steel, whereas ARU-TEN is almost free from red rust, showing excellent anti-rust resistance comparable to that of Type 304. **Figure 3** shows the maximum corrosion depth of each of the test samples coated with inorganic zinc rich primer. The corrosion depth of ARU-TEN is about 1/10 that of the mild steel and about 1/5 that of the 5%Cr steel. From the above results of CCT, it can be seen that when ARU-TEN is coated with inorganic zinc rich primer exhibits nearly the same corrosion resistance as Type 304.[9]

Table 1 Example of chemical compositions of ARU-TEN (mass%)

C	Si	Mn	P	S	Cr	Others
0.02	0.26	2.61	0.007	0.001	5.99	Al, Cu, Ni

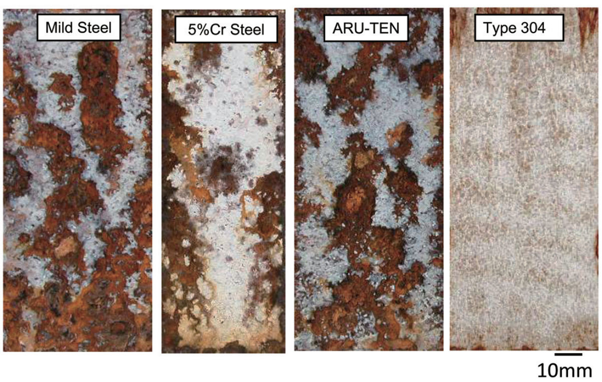

Fig. 1 Appearance of samples (bare surface) after corrosion test for 90 cycles [9]

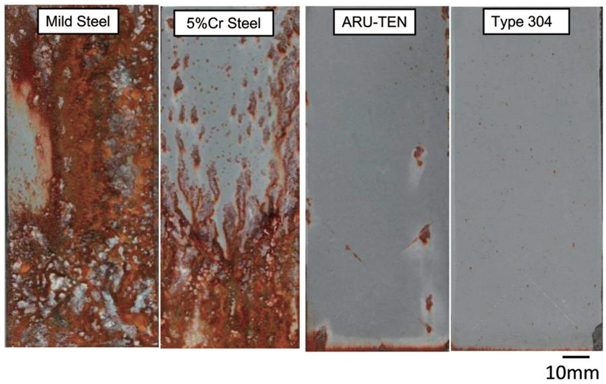

Fig. 2 Appearance of Zn-primer painted samples after corrosion test for 150 cycles [9]

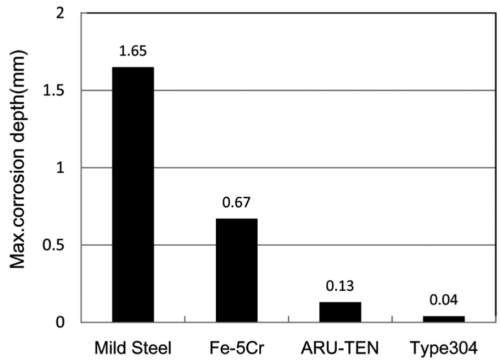

Fig. 3 Maximum corrosion depth of samples after corrosion test for 150 cycles [9]

2.2.2 Mechanism of high corrosion resistance of ARU-TEN

Figure 4 shows an example of pH measurement at the part of the steel surface where the Zn-based corrosion product was observed after the CCT. The measured pH was roughly 9 to 10, indicating that the zinc corrosion product was slightly alkaline. Considering that the weak alkalinity significantly helped restrain the occurrence of red rust on ARU-TEN coated with inorganic zinc rich primer, we measured the anodic polarization curves of each of the steel samples in a de-aerated quiescent solution of artificial seawater adjusted to a weak alkali. **Figure 5** shows the anodic polarization curves of the steel samples in artificial seawater adjusted to pH 9.2 by reducing the chloride concentration to 2/3 that of artificial seawater. The mild steel shows the behavior of active dissolution and the 5%Cr steel is slightly passivated before starting active dissolution. On the other hand, ARU-TEN shows a passive state wherein the current density does not increase with the rise of potential. This tendency of ARU-TEN is the same as that observed in the CCT. Namely, it is considered that the marked improvement in anti-rust resistance of ARU-TEN coated with inorganic Zn-rich primer is attributable to not the barrier effect of Zn-based product of corrosion but the passivation of ARU-TEN by the combined effect of the slightly alkaline Zn-based product of corrosion and the steel composition.[10)]

Figure 6 shows a typical example of the initial cross section of ARU-TEN after it was coated with inorganic Zn-rich primer. **Figure 7** shows an optical micrograph of the cross section of Zn-based corrosion product layer on ARU-TEN with inorganic zinc rich primer after CCT (ARU-TEN coated with inorganic Zn-rich primer containing a relatively large proportion of zinc and applied to bridges; 12 months after CCT). The initial cross section reveals metallic Zn particles 10 μm or less in size on average. After the CCT, the cross section shows very few metallic zinc particles and the steel surface is covered with a layer of Zn-based product of corrosion, which apparently helps prevent corrosion of the base metal. It can be seen that Zn, O, and Mg are distributed in the layer of product of corrosion (**Fig. 8**). The implication is that in the cyclic process of wetting and drying, a layer of Zn-based product of corrosion containing Mg compounds are formed, whereby the base metal surface becomes slightly alkaline.

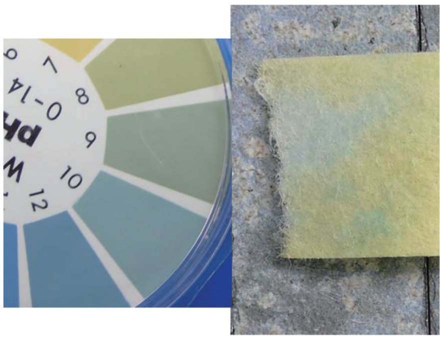

Fig. 4 Measurement result of pH on Zn-primer painted corrosion product after CCT

3. Corrosion Resistance of ARU-TEN in Mild Corrosive Environment (Indoors)

Even in an environment subject to severe salt damage, ARU-TEN exhibits good corrosion resistance when it is coated with an inorganic Zn-rich primer. On the other hand, it was considered that

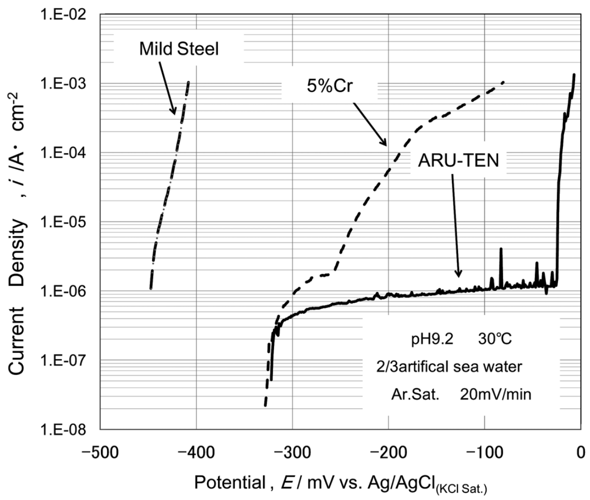

Fig. 5 Anodic polarization curves of mild steel, 5%Cr and ARU-TEN in mixed solution of artificial sea water and standard buffer solution, with its pH 9.2

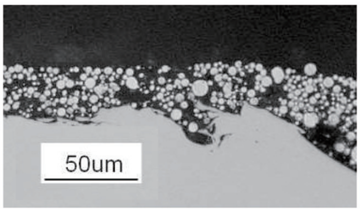

Fig. 6 Example of optical microphotographs of cross-section of Zn-primer painted samples (before test) (zinc content of heating residue: about 80%, aimed coating thickness 25 μm)

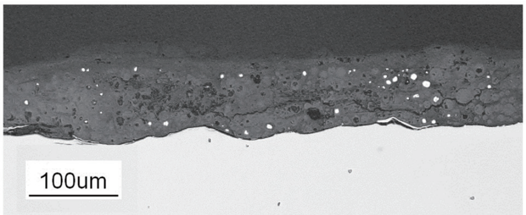

Fig. 7 Optical microphotographs of cross-section of rust layer on Zn-primer painted samples after CCT

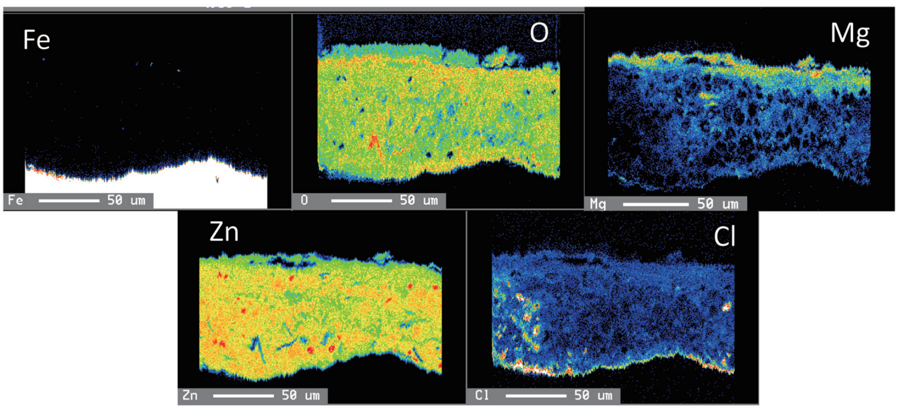

Fig. 8 EPMA analysis results of cross-section of rust layer on Zn-primer painted steel for after CCT

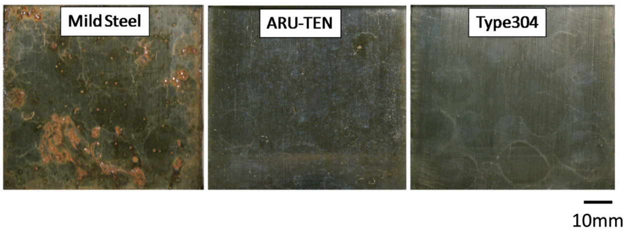

Fig. 9 Appearance of samples (bare surface) after condensation corrosion test for 300 h

in relatively mild corrosive environments with a low chloride concentration that are only subject to the cycle of wetting with dew during nighttime and drying during daytime, even unpainted ARU-TEN would display good resistance to red rust. Therefore, we studied the corrosion resistance of ARU-TEN without primer coating in such a mild corrosive environment.

The specimens used are 2.5 mm thick sheets of Mild steel, ARU-TEN, and Type 304, each measuring 75 mm by 75 mm. After their surface was subjected to a hairline finish, they were degreased, cleaned, and made into test samples. With the test samples set in position in the vapor-phase space of a thermostatic water tank, pure water in the tank was heated to 80°C and the test samples surfaces were kept wet with dew for 300 h. **Figure 9** shows the appearances of test samples after the 300-h corrosion test. The Mild steel revealed red rust, whereas ARU-TEN showed only tiny spots of rust that can hardly be identified macroscopically. Thus, it can be seen that in a mild indoor environment with a low chloride concentration, ARU-TEN is comparable in red rust resistance to Type 304.

4. Mechanical and Other Properties of ARU-TEN

4.1 Properties of base metal

4.1.1 Manufacturing process

The properties of ARU-TEN manufactured on a commercial production line are described below. The molten steel for ARU-TEN was refined by an ordinary converter and secondary refining equipment. The steel plates 4.5 mm to 25 mm in thickness were manufactured by the continuous hot rolling or plate mill with continuously cast slabs.

4.1.2 Mechanical properties

Table 2 shows mechanical properties of the base metal. The strength of the base metal of ARU-TEN is of the 490 MPa class and the Charpy absorbed energy at 0°C is 200 J or more.

4.2 Properties of weld zones

4.2.1 Weldability

Table 3 shows the conditions of a y-groove weld cracking test for a 25-mm-thick plate conducted in accordance with JIS Z 3158, and **Table 4** shows the test results. As the welding material, Type 309 stainless steel having good corrosion resistance was used. Even at 0°C, ARU-TEN was free from cold cracking, proving that it has good weldability.

4.2.2 Mechanical properties

Using the 12 and 25 mm thick plates, we examined the mechanical properties of welded joints. **Table 5** shows the welding conditions used and **Figure 10** shows the weld groove shape. With a type 309-based welding material having a wire diameter of 1.2 mm, each of the 12 and 25 mm thick plates was butt-welded by FCAW. The welding heat input was 1.3 to 1.4 kJ/mm. Neither preheating nor postheating was done.

Table 6 shows the results of a tensile test of the welded joints. The welded joints of both plates of ARU-TEN fractured under a tensile strength higher than 600 MPa that is close to that of the base metal.

Figure 11 shows the results of a Charpy impact test of the welded joints with a notch given to the weld metal, fusion line (FL), HAZ 1 (part 1 mm away from FL), and HAZ 3 (part 3 mm away from FL). Both plates show an absorbed energy exceeding 27 J at 0°C.

Figure 12 shows the measured hardness distribution along the cross section of a welded joint of the 25 mm thick plate. The hardness of the FL is somewhat high, whereas the hardness of the HAZ

Table 2 Mechanical properties of base plates

Plate thickness (mm)	Tensile properties				Impact property	
	Specimen type	Yield strength (N/mm^2)	Tensile strength (N/mm^2)	Elongation (%)	Specimen type	$vE_{0°C}$ (J)
4.5	JIS 5	488	620	29	–	–
9	JIS 5	437	686	27	–	–
12	JIS 1A	409	659	21	JIS V	204
25	JIS 1A	390	636	21		215

Table 3 Welding condition of y-groove weld cracking test

Plate thickness (mm)	Welding material	Current (A)	Voltage (V)	Speed (cpm)	Heat input (kJ/mm)
25	JIS Z 3323 YF309LC type	170	26	15	1.8

Table 4 Test results of y-groove weld cracking test

Condition		Cracking rate (%)								
Temperature (°C)	Humidity (%)	Surface			Cross section			Root		
		1	2	Ave.	1	2	Ave.	1	2	Ave.
20	60	0	0	0	0	0	0	0	0	0
0	–	0	0	0	0	0	0	0	0	0

Table 5 Welding condition

Plate thickness (mm)	Welding method	Welding material	Shield gas	Number of passes	Welding condition			
					Current (A)	Voltage (V)	Speed (cpm)	Heat iput (kJ/mm)
12	Flux cored arc welding	JIS Z 3323 (1.2mm φ) TS309L	Ar + 20%CO_2	5	210	27	26	1.3
25				BP: 5	210	26	25	1.3
				FP: 5	220	27	25	1.4

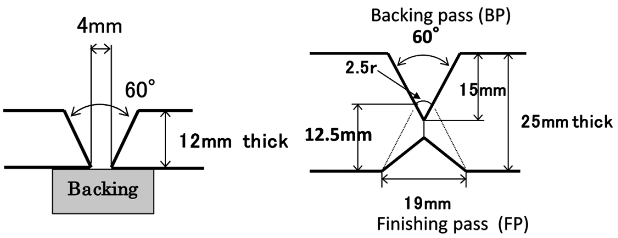

Fig. 10 Groove shape

Table 6 Test results of tensile test

Plate thickness (mm)	Tensile properties			
	Specimen type	Yield strength	Tensile strength	Lacation of fracture
12	JIS Z 3121 Type-1	521	648	Weld metal
		522	620	Weld metal
25		463	644	Weld metal
		465	633	Weld metal

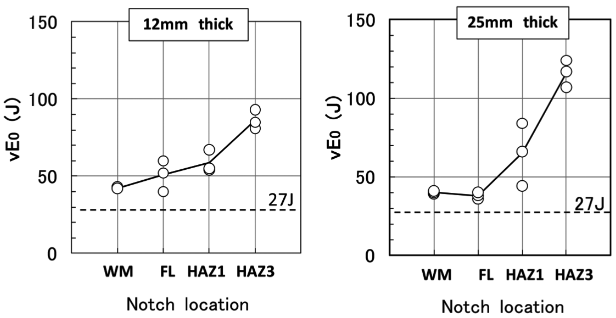

Fig. 11 Test results of Charpy impact test

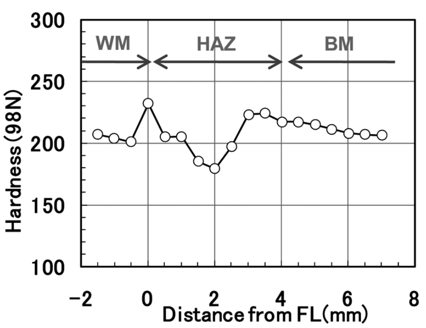

Fig. 12 Hardness distribution of welded joint (25 mm)

is somewhat low. Nevertheless, the difference in strength between them is not very conspicuous.

4.3 Other properties of ARU-TEN

4.3.1 Cuttability and machinability

When cutting ARU-TEN, it is desirable to use a plasma cutter or laser cutter. On the other hand, ARU-TEN is comparable in machinability to carbon steel and can be fixed by a magnet. Therefore, it is superior in tool life, machining speed, and working accuracy to Type 304 (**Fig. 13**). In addition, it has been confirmed that the machinability of ARU-TEN is equal or superior to that of Type 303 stainless steel that has better machinability than Type 304.

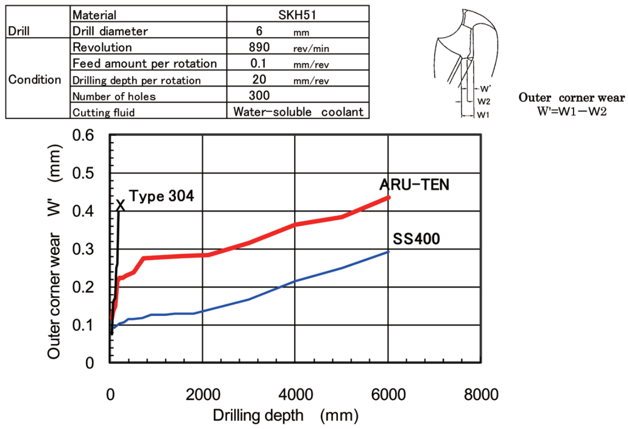

Fig. 13 Influence of materials on outer corner wear of drill tip

Table 7 Physical properties of ARU-TEN

Physical properties	(20°C)	SS400	Type 304	ARU-TEN
Elastic modulus	GPa	206	194	206
Co-efficient of thermal expansion	10^{-6}/°C	12	17	13
Thermal conductivity	W/m/K	58	16	22*
Specific heat	J/g/K	0.46	0.5	0.45
Electrical conductivity	$\mu\Omega \cdot$cm	16	72	72
Magnetism		Magnetic	Nonmagnetic	Magnetic

* 20–300°C

4.3.2 Physical properties

Table 7 compares the physical properties of ARU-TEN with those of SS400 and Type 304. The thermal conductivity and electrical resistance of ARU-TEN are close to those of Type 304. With respect to the other physical properties, ARU-TEN is nearly the same as SS400.

5. Specifications of ARU-TEN

The established specifications of ARU-TEN are shown in **Tables 8** and **9**. With respect to the chemical composition, Cr and Al have been added to improve the corrosion resistance, and the content of C has been somewhat lowered to restrain the precipitation of carbides of Cr. The content of Mn has been set with consideration given to the toughness of welded joints.

The standard plate thicknesses are between 6 mm and 25 mm. However, the manufacturable range is 2.3–50 mm. There are three grades of ARU-TEN: ARU-TEN-A has only a chemical composition specified but does not guarantee mechanical properties, ARU-TEN-B guarantees tensile test, and ARU-TEN-C guarantees tensile test and impact test.

6. Examples of Application of ARU-TEN to Industrial Equipment

Figure 14 shows ARU-TEN with inorganic Zn-rich primer coating applied to the duct of a vertical coal conveyor (PCI) of a steelworks. Located about 200 m away from the coast line, the steelworks is in an environment subject to severe salt damage. Although about 2.8 years have passed since installation, the duct still maintains a good appearance.[11] In addition, positive efforts are being made to widen the scope of application of ARU-TEN in highly corrosive environments, such as dust plates under the ore/coal conveyors of steelworks and equipment of plants located in coastal regions.

In relatively mild corrosive environments having a low chloride concentration and subject merely to the cyclic wetting with dew during nighttime and drying during daytime, even unpainted ARU-TEN can be expected to display good resistance to red rust. Therefore, the application of ARU-TEN to vacuum vessels, etc. is also being pressed ahead (**Fig. 15**).

7. Conclusion

We have come up with a new steel, ARU-TEN, that exhibits good corrosion resistance even in extremely corrosion environments. ARU-TEN permits reducing the amounts of addition of costly rare metals significantly since the steel surface is passivated through weak alkalinization by the action of a Zn-based corrosion product of the inorganic zinc rich primer coat and by the addition of such alloying elements as Cr and Al.

ARU-TEN is unique in that it is comparable in corrosion resistance to stainless steels and that it has good machinability and weldability close to those of carbon steels. It is expected that the application of ARU-TEN having those advantageous features to industrial plants located in coastal regions and precision equipment, etc. used indoors will expand in the future.

Acknowledgments

We wish to express our heartfelt thanks to Messrs. Keita Suzumura and Kazuo Goromaru of Nippon Steel & Sumitomo Metal Engineering Co., Ltd. for their generous cooperation in applying ARU-TEN to the vertical conveyor duct of the steelworks and to Messrs. Makoto Hanazawa and Mitsuo Iwasaki of Nippon Steel & Sumikin Texeing. Co., Ltd. for their enormous help with the application of ARU-TEN to indoor equipment.

Table 8 Chemical compositions of ARU-TEN

C	Si	Mn	P	S	Cr	T-Al	Others
≦ 0.05	≦ 0.55	≦ 3.00	≦ 0.035	≦ 0.035	≧ 5.50	≦ 1.10	Other elements may be added if necessary

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Table 9 Mechanical properties of ARU-TEN

Grade	Thickness (mm)	Yield point or Yield strength (N/mm²)	Tensile Strength (N/mm²)	Elongation			Charpy impact test (1/4 thickness-longitudinal direction)			
				Thickness (mm)	Test specimen	(%)	Thickness (mm)	Test temp. (°C)	Absorbed energy (J)	Test specimen
ARU-TEN-A	6 – 25 (2.3 – 50)	No test					> 12	No test		
ARU-TEN-B		≧ 315	490 – 700	≦ 16	JIS 1A	≧ 15				
				16 <	JIS 1A	≧ 19				
ARU-TEN-C				40 <	JIS 4	≧ 21		0	≧ 27	JIS V-notch

Fig. 14 Coal perpendicular conveyer duct of ARU-TEN

Fig. 15 Precision machinery (vacuum vessel) of ARU-TEN

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