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Materials Integrity Analysis for Application of Hyper Duplex Stainless Steels to Korean Nuclear Power Plants

Hyun-Young Chang[1,†], Heung-Bae Park[1], Yong-Soo Park[2], Soon-Tae Kim[2], Young-Sik Kim[3], Kwang-Tae Kim[4], and Yoon-Young Jhang[5]

[1]*Korea Power Engineering Company INC, Korea,* [2]*Yonsei University, Korea*
[3]*The Centre for Green Materials Technology, Andong National University, Korea*
[4]*POSCO, Korea,* [5]*ANSCO, Korea*
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Hyper duplex stainless steels have been developed in Korea for the purpose of application to the seawater system of Korean nuclear power plants. This system supplies seawater to cooling water heat exchanger tubes, related pipes and chlorine injection system. In normal operation, seawater is supplied to heat exchanger through the exit of circulating water pump headers, and the heat exchanged sea water is extracted to the discharge pipes in circulating water system connected to the circulating water discharge lines. The high flow velocity of some part of seawater system in nuclear power plants accelerates damages of components. Therefore, high strength and high corrosion resistant steels need to be applied for this environment. Hyper duplex stainless steel (27Cr-7.0Ni-2.5Mo-3.2W-0.35N) has been newly developed in Korea and is being improved for applying to nuclear power plants. In this study, the physical & mechanical properties and corrosion resistance of newly developed materials are quantitatively evaluated in comparative to commercial stainless steels in other countries. The properties of weld & HAZ (heat affected zone) are analyzed and the best compositions are suggested. The optimum conditions in welding process are derived for ensuring the volume fraction of ferrite(α) and austenite(γ) in HAZ and controlling weld cracks. For applying these materials to the seawater heat exchanger, CCT and CPT in weldments are measured.
As a result of all experiments, it was found that the newly developed hyper duplex stainless steel WREMBA has higher corrosion resistance and mechanical properties than those of super austenitic stainless steels including welded area. It is expected to be a promising material for seawater systems of Korean nuclear power plants.

Keywords *: hyper duplex stainless steel, nuclear power plants, CCT, CPT*

1. Introduction

Nuclear power generation currently occupies about 16% of whole electric power production in the world, and 436 units of nuclear power plants are producing 372 million kilowatt per year from 31 countries over the world(June, '08). In Korea, 20 units of nuclear power plants are being operated, 6 units are currently being constructed and 6 more units are scheduled to be constructed for ten years from now.

Nowadays, the issues related to the high oil prices, resource depletion and climate change are throwing the spotlight on introducing nuclear power plants in many countries. Owing to the global booming of nuclear power plants, IAEA forecasts maximum 228 of NPP units are expected to be constructed and WNA estimates maximum 312 units of NPP construction until year 2030.

From the construction prospects of nuclear power plants and thermal power plants, the demands of corrosion resistant alloys for the power plants can be estimated in the world materials market. It is estimated that power plants construction will creates demands for 1.2 million tons of super corrosion resistant alloys and 14 million tons of general corrosion resistant steels in the world market until year 2020 (Table 1). In this work, a material integrity analysis for application of hyper duplex stainless steels to Korean nuclear power plants was done.

2. Applicable environments and stainless steels

Fig. 1 shows the applicable environments of commercial ferritic, duplex and austenitic corrosion resistant alloys. In this Figure, Pitting Resistance Equivalent Number (PREN) can be also compared according to composition

† Corresponding author: hyjang@kepco-enc.com

Table 1. World market prospects of corrosion resistant steels for power plants

Materials \ Year		2008	2010	2012	2014	2016	2018	2020
Super corrosion resistant alloys[1)]	Amount (1000 tons)	358.4	779.9	864.3	948.6	1,032.9	1,117.2	1,201.5
	Cost (Million €)	4,050	8,810	9,770	10,700	11,700	12,600	13,600
Corrosion resistant steels[2)]	Amount (1000 tons)	10,859	11,422	12,016	12,543	13,306	14,005	14,748
	Cost (Million €)	4,290	5,370	6,540	7,770	9,230	10,800	12,500

1) Applying 11,300€/ton by the statistical yearbook of international trade & self analysis,
2) Assuming that corrosion resistant steels are consumed 1,580ton per a thermal power plant(500MW) and 2,700ton per a nuclear power plant(800MW).

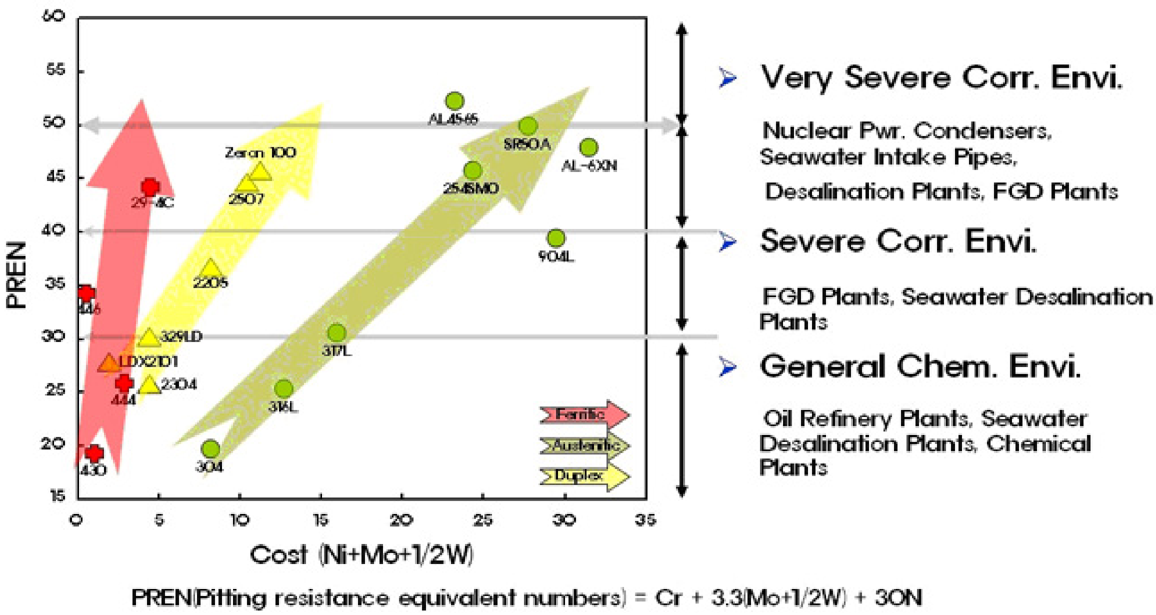


Fig. 1. Applicable environments as to the corrosion resistance of stainless steels.

of each alloy. As environments become severer, the materials of higher PREN should be applied. PREN values are practically used to predict corrosion resistance and its importance has been studied in many papers.[1)-7)]

Critical Crevice Temperatures (CCT's) as to PRENs of commercial corrosion resistant alloys are illustrated in the Fig. 2 in order to compare quantitatively corrosion resistance of them. Ranges of CCT (ASTM G48 Practice B) or PREN in some alloys in Figure come from the differences in data that various institutes or countries have acquired. This Figure, nevertheless, shows the linear proportionality between corrosion resistance and PREN of the corrosion resistant alloys.

Duplex stainless steels have a weak point that their weld heat affected zones have decreased corrosion resistance due to the precipitation of σ phase, etc. However, excellent mechanical properties and corrosion resistance of duplex stainless steel matrix have attracted many researchers to alleviate its shortcomings. SAF 2507 and UR52N+, etc. are the most superior duplex stainless steels that have been commercialized until now. These were dubbed as the 2nd generation duplex stainless steels or super duplex stainless steels in comparison with SAF 2205 and UR45N+ etc. that had been early developed.

Newly developed duplex stainless steels have been appeared recently that their mechanical properties and corrosion resistance had been one-step more improved from the 2nd generation duplex stainless steels. These steels are

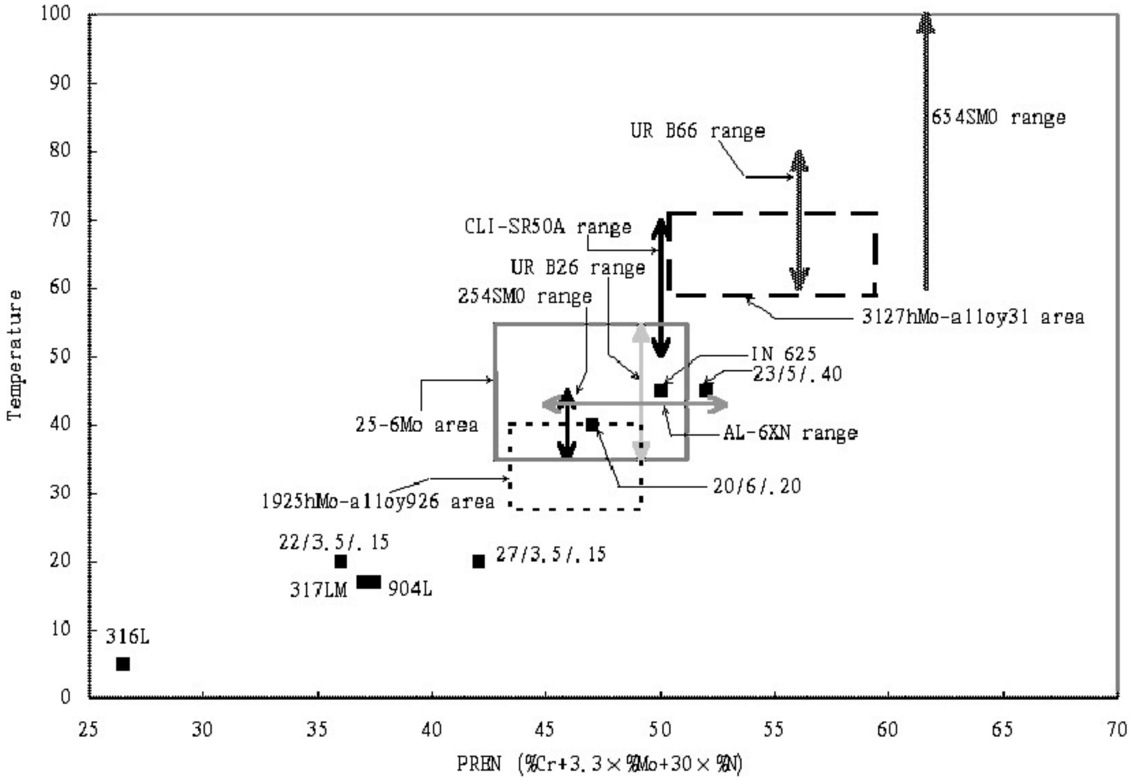


Fig. 2. Critical Crevice Corrosion Temperatures of commercial alloys as to their PREN.

Alloy		℃
Type 316L		-3
The 1st Generation	SAF 2205 Duplex	20
The 2nd Generation	SAF 2507 Super Duplex	35
The 2nd Generation	AL-6XN, UR B26 6-Mo Super Austenitic	43
	SR-50A 6-Mo Super Austenitic	50
The 3rd Generation	Hyper Duplex WREMBa	> 55

The 1st Gen. Stainless Steel : PREN 〈 40

The 2nd Gen. SS(Super Stainless Steel) : PREN ≥ 40

The 3rd Gen. SS(Hyper Stainless Steel) : PREN ≥ 50

Fig. 3. Classification of corrosion resistance alloys according to CCT and PREN.

called the 3rd generation duplex stainless steels or hyper duplex stainless steels. As shown in Fig. 3, the 3rd generation duplex stainless steels have not less than 90 ℃ of CPT and not less than 55 ℃ of CCT, a yield strength of 680 MPa and a tensile strength of 830 MPa, of which overwhelm those of 2nd generation duplex stainless steels such as SAF 2507, UR 52N+, ZERON 100 etc. (PREW 46 class steels). They are in the spotlight because of their exceeding properties over expensive 6Mo-super austenitic stainless steels (SR-50A, AL-6XN, 254SMO etc.).

The reason that these super or hyper duplex stainless steels are being concerned as materials for power plants is that they have enough price competitiveness even as a form of solid plate (t ≤ 6 mm) not a lining form for seawater system pipes compared to super austenitic stainless steels.

All of nuclear power plants in Korea are located in seashores and they are using seawater as cooling medium. Many nuclear power plants in Korea have had applied carbon steels + rubber lining or Archcoat™(fiber-glass reinforced coating) + cathodic protection to the pipes of circulating water systems including up to 84inch diameter pipes.

Sometimes these large diameter seawater pipes have

Fig. 4. Localized corrosion propagation after coating failures in seawater pipes.

Fig. 5. Localized corrosion damages after rubber liner failures in seawater valves.

been experienced coating failures from blistering caused by coatings deterioration or over-protection currents from cathodic protection systems. The localized corrosion such as pitting has been inevitability following these coating failures shown in Fig. 4. Another case history in the circulating water system shows the pitting damages in a large diameter valve shaft which is a rubber lined precipitation strengthened martensitic stainless steel(17-4PH), as shown in Fig. 5.

Therefore, it may not a good option to select low corrosion resistant steels with polymeric coatings for the extended durability of components in seawater systems. It'll be desirable to apply solid materials that have corrosion resistance and excellent mechanical properties in order to improve life extension and integrity, to decrease maintenance costs of components in seawater systems. Economic efficiency, of course, should be considered in advance.

There are seawater systems in a nuclear power plant as follows:

- Essential Service Water System (ESWS) supplies cooling seawater to component cooling water heat exchangers that are designed to operate with maximum temperature of 88.2 ˚F (31.2 ℃) cooling water..
- Turbine Building Open Cooling Water System (TBOCW) supplies seawater to heat exchangers, related pipes and chlorination system. Seawater is supplied from the common headers of circulating water pump behind and then heat exchanged seawater is released through discharging pipes connected to circulating water discharging line.
- Circulating Water System (CWS) removes waste heat from the condensers and supplies seawater to sustain pressures of condensers. CWS, which is an auxiliary facility of the steam generator, discharges absorbed waste heat into the sea.

Therefore, seawater systems in nuclear power plants could be selected as locations that require high strength and high corrosion resistant alloys because of high flow velocity (pumps, valves, condenser tubes etc.) and high probability of corrosion damages (Fig. 6).

Fig. 7 displays the materials selection criteria for seawater systems of power plants in Korea based on chloride concentration and pH.

The 3rd generation duplex stainless steel (WREMBa) which has been developed in Korea has superior corrosion resistance to the 2nd generation duplex stainless steels and super austenitic stainless steels. This alloy shows even equivalent corrosion resistance with expensive nickel based alloys (ex. Alloy 625, alloy C-276 etc.) or titanium alloys as well as shows excellent mechanical properties as shown later. It is expected that this alloy can be replaced as materials for seawater system, FGD (Flue Gas Desulphurization) system, petrochemical industry and paper manufacturing industry, etc.

Realistic criteria should be established for new materials such as a newly developed hyper duplex stainless steel to be applied to pipes or tubes of seawater systems in Korean nuclear power plants. For example, the temperature of intake seawater in circulating water system including condensers ranges -2.4~28.7 ℃, and the temperature of discharged seawater reaches maximum 43.5 ℃ (based on the shell side of condensers) after heat exchanging. Because almost all components and pipes may have crevices (ex, between tubes and sheets of condensers), the criteria for materials selection needs to be considered based on CCT. Solutions of ASTM G48 practice B or D (6% $FeCl_3$) and F (6% $FeCl_3$ + 1%HCl) can be considered a severer condition for test alloys compared to seawater

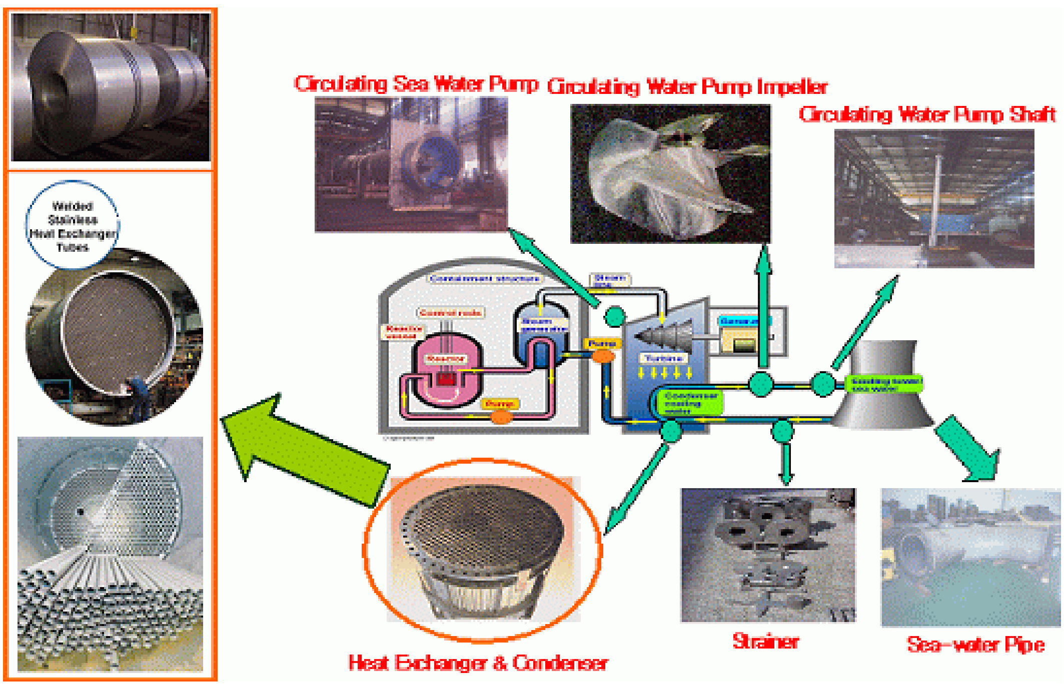


Fig. 6. Applicable components of super corrosion resistant alloys for seawater systems in nuclear power plants.

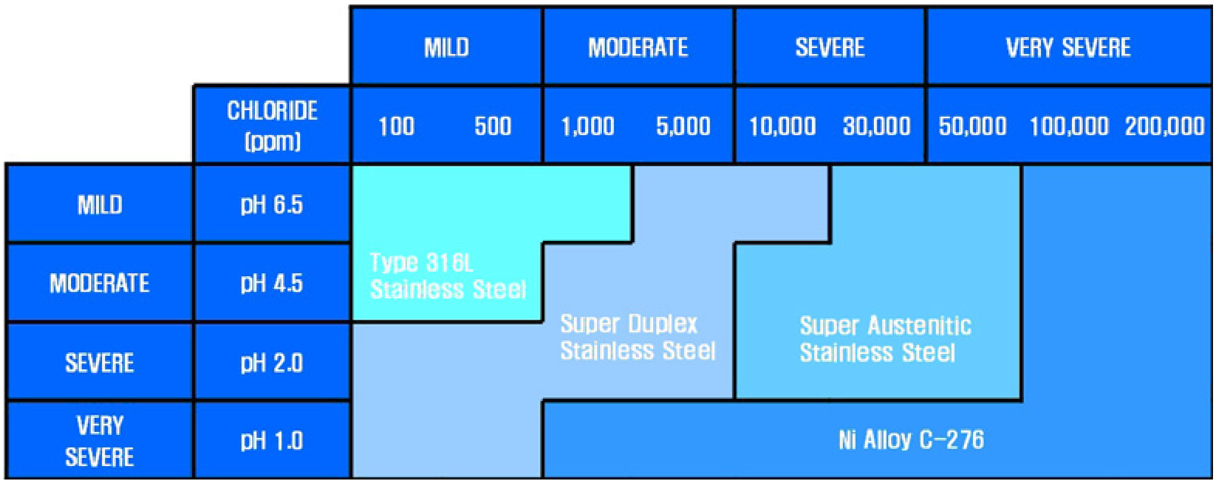


Fig 7. Materials selection criteria for seawater systems of power plants in Korea.

(3.5wt% NaCl).

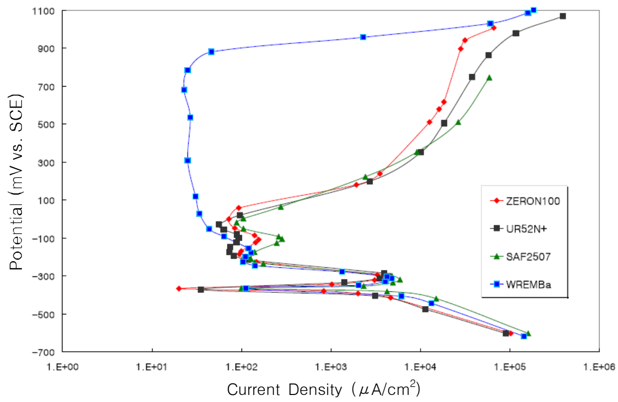
Therefore, the requirement of CCT ≥45 ℃ for materials application may be enough to be conservative. There should be no differences for applying criteria to matrix and weld area of materials, but it is difficult to perform CCT test in weld area of real components considering their geometries, leaving needs for further studies. Sometimes CCT can be induced from interrelationship between CCT and CPT. For example, there are differences of about 35 ℃~40 ℃ between ASTM G48 practice C (CPT) and D (CCT). However, there are uncertainties in criteria based on CPT, which also leaves room for further researches.

3. Materials integrity analysis of applicable stainless steels

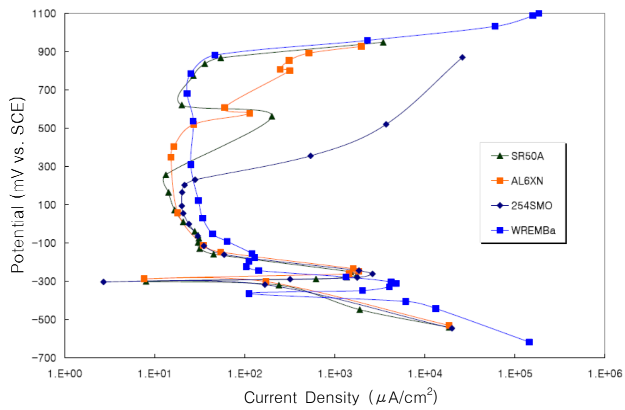
3.1 Corrosion resistance

Fig. 8 shows potentiodynamic anodic polarization curves of the 3rd generation duplex SS, 2nd generation commercial duplex SS and austenitic SS that are performed in the solution of 0.5N HCl+1.0N NaCl at 70 ℃. WREMBa of PREW 50 class in which rare-earth metal (REM) and Ba (barium) are added shows a lower passive current density and a higher pitting potential than those of other 2nd generation duplex SS, which means WREMBa has superior corrosion resistance to others. Moreover, its passive film is analyzed to be more stable than those of expensive commercial super austenitic SS, which also contributes to the excellent corrosion resistance.

In Fig. 9, the results of CPT based on ASTM G48 Practice A (10% $FeCl_3 \cdot 6H_2O$) and CCT conforming to ASTM G 48 Practice D(10% $FeCl_3 \cdot 6H_2O$+1%HCl) are presented for alloy WREMBa and other commercial



(a) Comparison with 2nd generation duplex stainless steels



(b) Comparison with commercial 6-Mo austentic stainless steels

Fig. 8. Potentiodynamic anodic polarization behavior for newly developed Korean hyper duplex stainless steel, the commercial super duplex steels and super austenitic stainless steels in deaerated 0.5N HCl + 1.0N NaCl at 70℃.

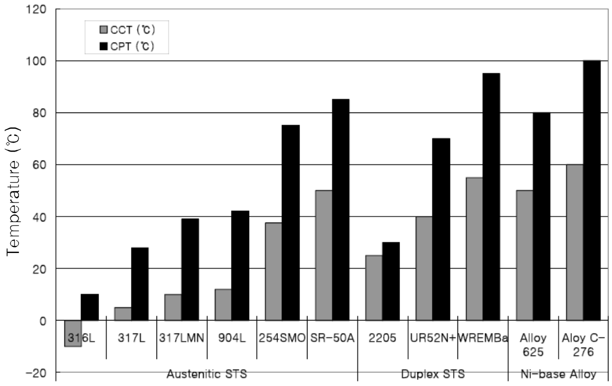


Fig. 9. Critical pitting & crevice temperature of newly developed Korean hyper duplex stainless steel and other commercial alloys per ASTM G48 practice A & D.

alloys. From the results, it can be verified that WREMBa is highly localized corrosion resistant from the higher CPT and CCT than those of super duplex SS (UR52N+) and super austenitic SS(254SMO, SR-50A). It also shows surprisingly equivalent corrosion resistance with nickel based alloys (Alloy 625, Alloy C-276)

3.2 Mechanical properties

WREMBa is based on the basic composition of Fe-27%Cr-7%Ni-2.5%Mo-3.2%W-0.35N in which REM and Ba are added to suppress the precipitation of 2nd phases that are harmful for the properties of duplex stainless steels. The results of mechanical properties are shown in Fig. 10 ~ Fig. 13 comparing with alloy WBASE (Fe-27%Cr-7%Ni-2.5%Mo-3.2%W-0.35N) and 45Mo(Fe-25%Cr-7%Ni-4.5%Mo-0.25%N). The hardness values decrease as the time of aging treatment increases, but hardness increases in case of 30 minutes aging treatment as shown in Fig. 10. It can be explained that this tendency comes from the vulnerable phases (σ or χ phases) that are trans-

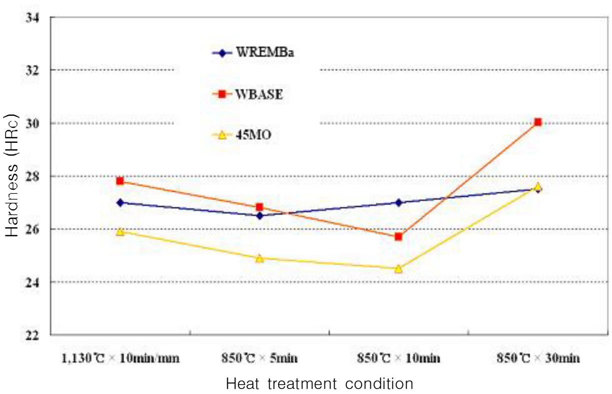


Fig. 10. Hardness changes of experimental alloys after aging treatment.

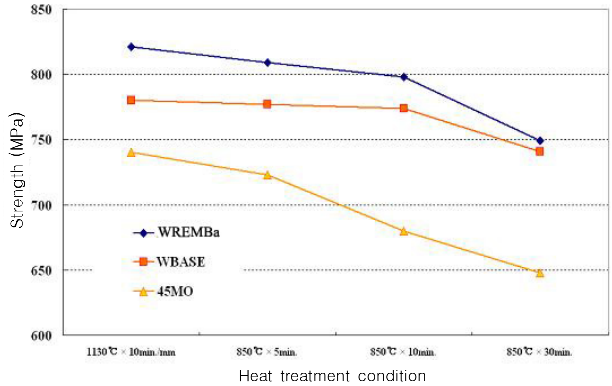


Fig. 11. Tensile strength changes of experimental alloys after aging treatment.

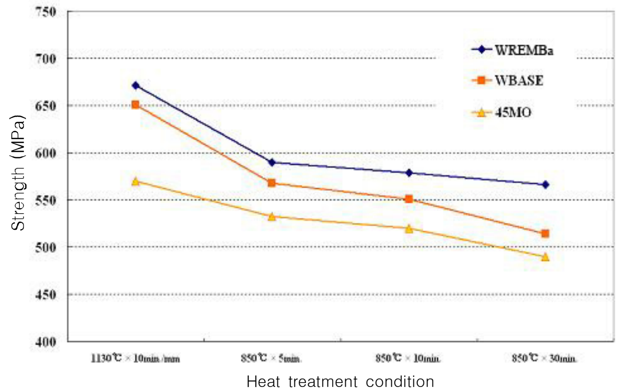


Fig. 12. Yield strength changes of experimental alloys after aging treatment.

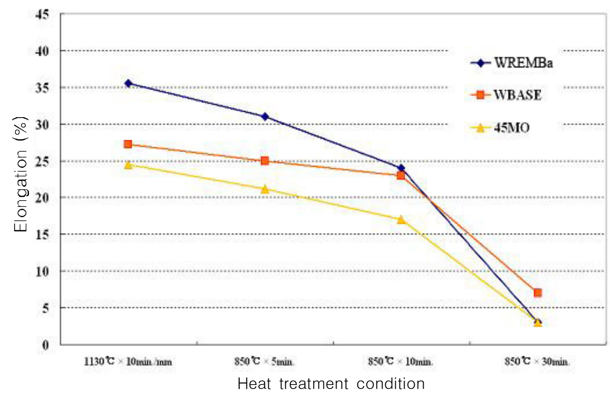


Fig. 13. Elongation changes of experimental alloys after aging treatment.

formed from σ phase.[8] However, the alloy in which REM and Ba are added shows the decreased differences of hardness between in aging treatment and in solid solution treatment. This means that σ phase and χ phase precipitation decrease in aging treatment. Furthermore, the duplex stainless steel with REM and Ba shows excellent mechanical properties from tensile tests shown in Fig. 11 ~ Fig. 13, which can be explained from the theory that minute REM oxides and Ba oxides have effectively pinned phase or grain boundaries resulting in refining the sizes of austenite and ferrite phases.[8)-14)]

3.3 Welding properties

In order to evaluate the welding properties of WREMBa with a function of heat input, microstructures are analyzed and corrosion resistance is evaluated after specimens are welded with GTAW method. As shown in Fig. 14, the photos of the optical microscope and scanning electron microscope back scattering reveal that WREMBa with REM and Ba produces sound microstructures with little

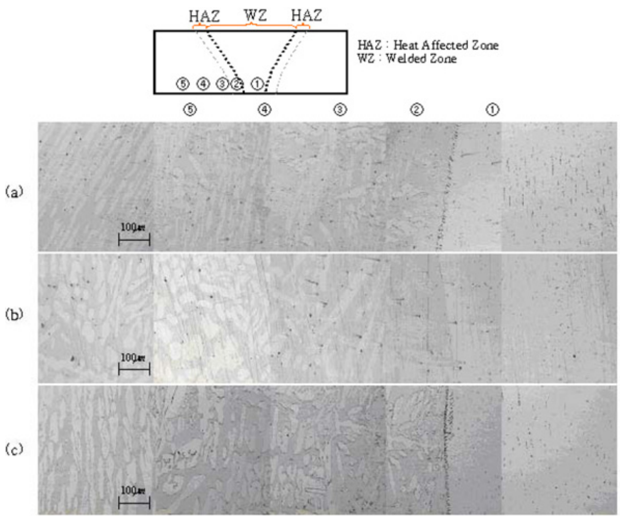


Fig. 14. Optical micrographs of the experimental alloys welded by GTAW method.
(a) WREMBa, 1.0kJ/mm, (b) WBASE, 1.0kJ/mm, (c) 45MO, 1.0kJ/mm

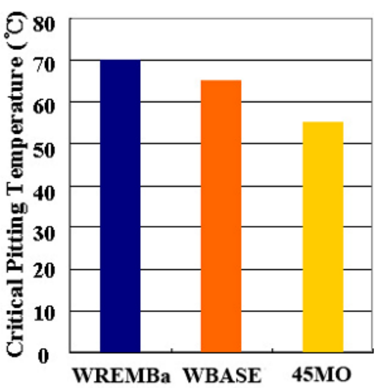


Fig. 15. Critical pitting temperatures of the experimental alloys welded with heat input of 1.0kJ/mm by GTAW method.

precipitation of the 2nd phases. Although heat input increases, the CPT of heat affected zone(HAZ) in welded WREMBa specimen reaches to as high as 70 ℃ as shown in Fig 15. This results are attributed to the fact that REMs of large diameter or fine REM oxides with diameters of 1~3 ㎛, and Ba oxides or sulfides delay diffusion of Cr, Mo and W species.[14)]

4. Prospects for hyper duplex stainless steels

The 1st generation duplex stainless steel, SAF2205 has been mainly being produced in Korea, which has lower corrosion resistance and mechanical properties. Although the 2nd generation duplex stainless steel, SAF2507 is about to be mass-produced, but it has a problem that production recovery rates are considerably decreased owing to the inadequate production process conditions such as melting, casting, heat treatment, maintenance welding and cutting manufacturing. These process conditions are important for ensuring the best corrosion resistance and mechanical properties.

The newly developed WREMBa, in the mean time, is expected to be a promising material for Korean power plants. This alloy has higher pitting and crevice corrosion resistance than super austenitic stainless steels. Its yield strength is 1.8 times higher and it has 11 - 17% lesser Ni contents contributing to lower prices than those of super austenitic stainless steels. In case of setting up appropriate quality assurance procedures in manufacturing process, it is anticipated that WREMBa can be replaced in the area of applying super austenitic stainless steels, alloy 625 and C-276 (Table 2).

4. Conclusions

Excellent mechanical properties and corrosion resistance of duplex stainless steel matrix have attracted many researchers to alleviate its shortcomings. Hyper duplex stainless steels have enough price competitiveness compared to expensive super austenitic stainless steels because they have less expensive alloying elements. From the experimental data of mechanical properties and corrosion resistance, it was found that the WREMBA had superior mechanical properties and corrosion resistance comparing to super austenitic stainless steels in seawater environments. This hyper duplex stainless steel, in the mean time, has better welding properties than that of traditional duplex stainless steels due to less precipitation of vulnerable phases such as σ phase. This alloy is expected to be a promising material for seawater systems in nuclear power plants.

Table 2. Comparison of WREMBa with other commercial duplex, austenitic stainless steels and Nickel based alloy

Material Item		Duplex Stainless Steel			Austenitic Stainless Steel		Ni-base Alloy
		WREMBa	UR 52N+	SAF 2205	SR 50A	AISI 316L	Alloy 625
Chemical composion(wt%)		Fe+27Cr+ 7.0Ni+2.5Mo 3.2W +0.35N +0.02C	Fe+25Cr+ 6.5Ni+3.6Mo +0.25N +1.5Cu +0.02C	Fe+22Cr+ 5.3Ni+2.8Mo +0.16N +0.02C	Fe+23Cr+ 21Ni+6.2Mo +0.28N +0.03C	Fe+17Cr+ 12Ni+2.5Mo +0.03C	Ni+21.5Cr+ +9Mo+<5Fe +4Nb +<0.06C
PREW		51.3	44.4	36.1	51.9	25.3	51.2
Mechanical property	Y.S (MPa)	560 ≤	550 ≤	450 ≤	330 ≤	170 ≤	276 ≤
	T.S (MPa)	780 ≤	760 ≤	620 ≤	675 ≤	485 ≤	690 ≤
	El.(%)	25 ≤	15 ≤	25 ≤	40 ≤	40 ≤	30 ≤
	Hardness(HB)	310 ≥	302 ≥	293 ≥	250 ≥	217 ≥	230 ≥
Wear resistance		WREMBa > UR52N+ > SAF 2205 > SR 50A > AISI 316L ≒ Alloy 625					
Corrosion property	CPT(6% $FeCl_3$)	90 - 95℃	40 - 70℃	≤30℃	70 - 90℃	10℃	70 - 90℃
	CCT(6% $FeCl_3$)	55℃	30 - 40℃	17 - 30℃	50℃	-10℃	35 - 50℃
	Pitting & Crevice corrosion resistance	WREMBa > SR 50A ≒ Alloy 625 > UR52N+ > SAF 2205 > AISI 316L					
	Erosion corrosion resistance	WREMBa > SR 50A ≒ Alloy 625 ≒ UR52N+ > SAF 2205 > AISI 316L					

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