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Development of New High-Performance Stainless Steels

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This paper focused on high-performance stainless steels and their development status. Effect of nitrogen addition on super-stainless steel was discussed. Research activities at Yonsei University on austenitic and martensitic high-performance stainless, steels, and the next-generation duplex stainless steels were introduced.

Keywords : *Super-stainless steel, austenite, martensite, duplex stainless steel*

1. Introduction

Since its inception as 12% Cr steel, stainless steel has found itself wide application in our everyday life. Recent industrialization has led to rapid deployment of fossil power plants, nuclear power plants, petrochemical plants, water treatment plants, and various waterfront facilities, just to name a few, and along with it, accompanying construction technology is advancing with speed.

However, these structures utilize carbon steel, zinc galvanized steel, copper alloys, or common stainless steel, which face a shortened life-span and require frequent repairs in our new harsh environment found with heavily polluted waste water, industrial waste waters, and sewage. As replacement of these old facilities are inevitable, supply of new and highly corrosion-resistance metals are in great need.

Usage of metals in aquatic environment naturally has constraining factors that limit the layout design of the industrial facility : crevice corrosion, pitting corrosion, stress corrosion cracking, hydrogen embrittlement, intergranular corrosion, erosion corrosion. Super-stainless steel overcomes these corrosion conundrums, providing tensile strength, yield strength, and impact toughness. Super-stainless steel also inherits Life Time vs. Cost advantage and reliability.

To counter the aforementioned deterioration by corrosion, research started at the end of the 1970's, adding N and Mo to greatly enhance passive film. We have been researching in the areas of the austenite, duplex, and martensite stainless steels, and are now applying the newly acquired technology in various facilities.

This presentation will focus on these types of high-performance stainless steel, and their development status.

2. Development of new super and high-performance stainless steels

2.1 Definition of super-stainless steel

Today, Super-Stainless Steel, or High-Performance Stainless Steel refers to stainless steel with much improved corrosion resistant characteristics. This may also be called Super Corrosion- Resistant Stainless Steel due to its obvious characteristics. Exactly what level of corrosion resistance is required to qualify as super-stainless steel is an important question.

Factors that contribute to reducing pitting corrosion, crevice corrosion, stress corrosion cracking, corrosion fatigue, hydrogen embrittlement, intergranular corrosion do so by generating dense and strengthened passive film, high strength, austenitic characteristics, and low carbon content in the stainless steel. Generation of strengthened passive film not only enhances pitting corrosion and crevice corrosion resistance, but also suppresses stress corrosion cracking, and therefore is the most important feature.

This strength of passive film may be percisely rated by ensuring the amount of Cr, Mo, etc. which contributes to the formation of passivity. Garner-derived Cr-Equivalent equation[1)] (%Cr + 3.3%Mo) is first of such measurement methods. For nitrogen bearing stainelss steels, Heubner et al.[2)] and Rockel et al.[3)] showed that critical pitting temperature(C.P.T.) increased with pitting resistance equivalent(P.R.E. : %Cr + 3.3%Mo + 30%N) (Figure 1). Because the P.R.E. was expressed as (%Cr + 3%Mo + 70%N) by Ujiro et al.[4)] in 1991(Figure 2), there seemed to be no universal agreement on the exact expression for P.R.E. However, it became known when P.R.E. value is somewhat above 40, the particular stainless steel has

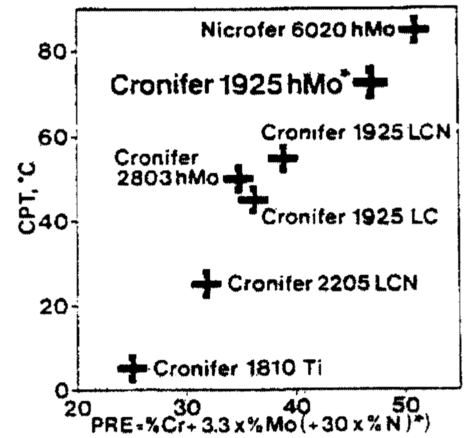


Fig. 1. Critical pitting temperature of high alloyed stainless steels after 24h testing in 10% $FeCl_3$ as a function of pitting resitance equivalent(P.R.E.)

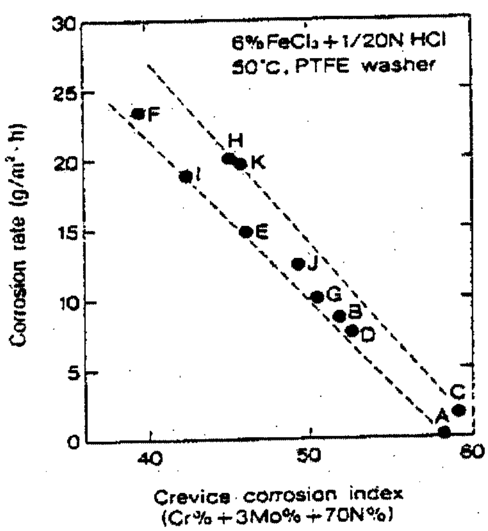


Fig. 2. Relation between crevice corrosion rate and crevice corrosion index (%Cr+3%Mo+70%N)

superior resistance to pitting corrosion and crevicecorrosion. So, when a Mo and N containing stainless steel displays a strong P.R.E., with value of 40 or above, it is categorized as super-stainless steel.

2.2 Effect of nitrogen addition

Since 1981 the Corrosion Research Group at Yonsei University has steadily studied nitrogen-containing stainless steel, and results thus far are as follows. When Cr content is at 23% and Mo and N are present at appropriate levels, they produce a synergistic effect, strengthening passive film.

Stress corrosion cracking resistance is high when nitrogen content ranges 0.21 - 0.25%. As increase in nitrogen level leads to a slow down of carbonization,

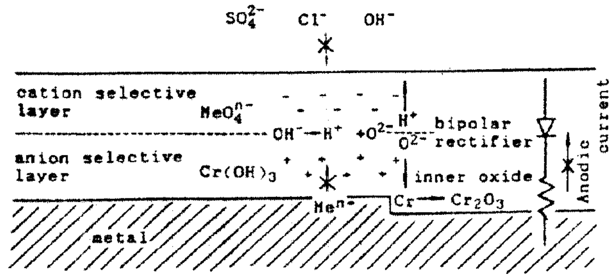


Fig. 3. Schematic representation of the bipolar model of the passive film formed on stainless steel (Positive fixed charge : +, Negative fixed charge : -).

esistance to sensitization is heightened. As nitrogen content increases, tensile strength, yield strength and hardness increase without losses in ductility and ferrite formation is suppressed, resulting in less susceptibility to Hydrogen Embrittlement.

Nitrogen and Mo addition effect on passive film strengthening may be explained as follows. More significant than either the effect of N or Mo alone, the combination of the two produces a synergistic effect towards enhancing the corrosion resistance of stainless steel. According to recent studies,[5,6] when nitrogen and Mo are both present, the desired effect of corrosion resistance is attained as passive films strengthened. Thus, when passive film was analyzed on the basis of XPS study, Cr, Mo, and Fe were found to concentrate on the outer layers of film, and this was especially true for Mo.

This, when viewed in terms of passive film' s Bipolar Model(Figure 3), is as follows. As passive film is formed of oppositely charged layers with positive charged outer layer and negative-charged inner layer the resistance characteristic is dramatically enhanced. When in a corrosive, low pH environment, OH^- ions are concentrated on the outer layers of passive film, generating inhibitive NO_3^-, $MoO_4^=$ ions. These negatively charged ions cause dehydration reaction ($OH^- \rightarrow H^+ + O^=$) which produces $O^=$ ions that are drawn to the positive charged inner layer. This increases the Cr_2O_3/CrOOH ratio and the total oxidation that leads to formation of dense passive film. Especially as N content increases and Mo is alone present in the alloy $O^=$is generated in even greater numbers than MoO_4^- in passive film. Their attraction of positively charged elements dramatically increases the corrosion resistance characteristics due to the aforementioned phenomena. This synergistic effect suggests a new kind of P.R.E, containing a product term of Mo and N(i.e. : Mo×N). This suggestion was confirmed later by Jargelius-Petterson[6] in 1998 [P.R.E. = %Cr + 3.3%Mo + 36%N + 7(%Mo)×(%N) - 1.6%Mn].

Table 1. Commercial Super Stainless Steel in the world

	Manufacturer	Brand Name	Chemical Composition	PRE
Austenitic STS	Avesta (Sweden)	254 SMO	Fe-20Cr-18Ni-6Mo-0.2N-0.7Cu	46.5
	Allegheney Ludlum (USA)	AL - 6XN	Fe-20.5Cr-24Ni-6.3Mo-0.22N-<0.75Cu	47.9
	INCO (USA)	25-6MO	Fe-20Cr-25Ni-6.5Mo-0.2N-1.0Cu	47.5
	CLI (France)	UR B-26	Fe-20.5Cr-25Ni-6.3Mo-0.2N-1.0Cu	47.3
	Kawasaki Steel (Japan)	-	Fe-22Cr-17Ni-4.5Mo-0.3N	45.8
	VDM (Germany)	Cronifer 1925hMo	Fe-21Cr-25Ni-6.4Mo-0.2N-0.9Cu	48.1
	Outokumpu Oy Polarit (Finland)	Polarit 778	Fe-20Cr-22Ni-6Mo-0.2N- 0.75Cu	45.8
	Korea	SR - 50A	Fe-23Cr-21Ni-6.2Mo-0.25N-<0.4Cu	51
Duplex STS	Cabot (USA)	Ferralium 255	Fe-25Cr-5Ni-2.8Mo-0.16N	39
	Sandvik (Sweden)	SAF 2507	Fe-25Cr-7Ni-3.8Mo-0.28N	45.9
	CLI (France)	UR 52N+	Fe-25Cr-6.5Ni-3.6Mo-0.25N-1.6Cu	44.4
	CLI (France)	UR 45N	Fe-21Cr-5.3Ni-2.8Mo-0.16N	36
	Sandvik (Sweden)	SAF 2205	Fe-22Cr-5.5Ni-3Mo-0.15N	36.4
	Korea	SR-6DX	Fe-23.2Cr-8.2Ni-5.7Mo-0.33N	51.9
Ferritic STS	Allegheney Ludlum (USA)	AL 29 - 4C	Fe-29Cr-4Mo-0.5Ti	42.2
	Trent Tube (USA)	SEA - CURE	Fe-27.5Cr-3.5Mo-1.2Ni- 0.4Ti	39
	Nyby - Uddeholm (Sweden)	MONIT	Fe-25Cr-4Ni-4Mo	38.2
	New Nippon Steel Co (Japan)	-	Fe-25Cr-4Mo-4Ni	38.2

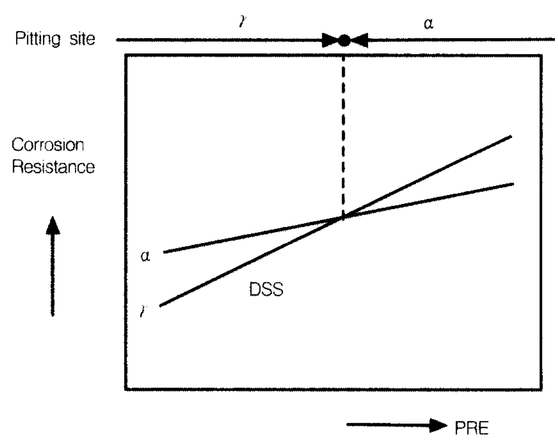
* PRE (Pitting Resistance Equivalent) = %Cr + 3.3 X %Mo + 30 X %N

2.3 Current status of high-performance stainless steel developed at Yonsei University

Development and application of super-stainless steel started in the early 1980's in the Unites States and Sweden, and were followed by other countries. Austenite stainless steel in particular due to its excellent corrosion resistance, ductility, and resistance to low-temperature embrittlement, is widely utilized in fossil power plants, nuclear power plants, waterfront facilities, pulp paper industry, FGD systems, and water treatment plants.

However, duplex stainless steel, while not as corrosion resistant as austenite, displays superior tensile and yield strength, and is suitable for work requiring both corrosion wear resistance and corrosion resistance.

Our research group has developed a new duplex stainless steel that far exceeds the corrosion resistance and mechanical characteristics of existing super duplex stainless steel, and also exceeds that of the austenite stainless steel. We have yielded world's first 65/35 (austenite/ferrite) ratio duplex stainles steel which, compared to other duplex stainless steels' 50/50 make-up, has superior machinability and corrosion resistance. Even



	Cr	Ni	Mo	N	W	PRE*
γ phase	22.5	10.3	4.2	0.45	1.2	51.8
α phase	24.4	6.7	6.5	0.05	2.2	51.0

*PRE(Pitting Resistance Equivalent) = %Cr + 3.3(%Mo + 0.5%W) + 30%N

Fig. 4. The Chemical Compositions of γ and α phases in SR-6DX and the phase ratio of 65% γ and 35 % α showing exact balancing of corrosion resistance.

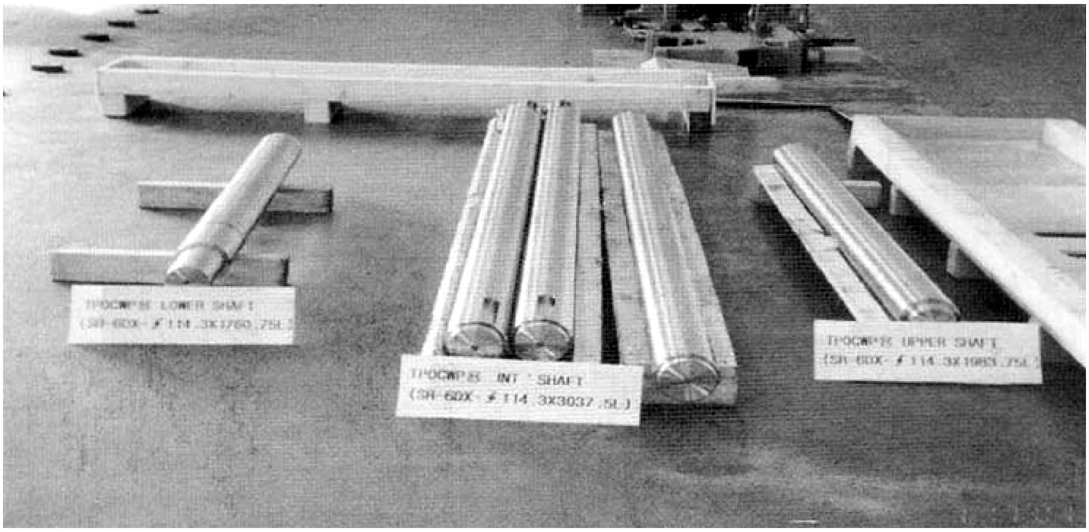


Fig. 5. SR-6DX super duplex stainless steel shaft supplied to Yeong Gwang Nuclear Power Plant (Jan. 2001)

though the corrosion resistance enhancing factors added are similar, this optimized ratio means much superior product is obtained. The grade(SR-6DX) is now patented in Korea, U.S., Europe, Japan, and China. For application of this new stainless steel, our research group in conjunction with some Korean foundary manufacturers and Scana of Norway began the work to produce commercial samples. Figure 5 shows SR-6DX super duplex shaft supplied to Yeong Gwang Nuclear Power Plant.

2.4 Comparison of super stainless steel characteristics

2.4.1 SR-50A super austenitic stainless steel

SR-50A is the first austenitic grade developed in our laboratory with improved corrosion resistance compared to conventional 6-Mo super stainless steel(Table 2). This grade is selected as one of the most cost effective stainless steel by CLi of Usinor group. The grade was assigned the UNS designation S32050 by ASTM and SAE societies in 1996, and introduced in Jan./Feb., 1997-issue of "Stainless Steel World". This alloy is particularly well designed for sea-water applications and pollution control equipments, and the chemistry is balanced to obtain an austenitic microstructure which explains the high toughness properties, including at -196℃(-320°F).

2.4.2 SR-3MO martensitic stainless steel with high corrosion resistance

SR-3MO is a martensite stainless steel developed in a government-sponsored project. In terms of the P.R.E. value it does not qualify as a super stainless steel (must

Table 2. Comparison with other commercial 6-Mo austenitic grades

		SR-50A (Korea)	UR B26 (France)	AL-6XN (U.S.A.)	1925hMo (Germany)	25-6MO (U.S.A.)	254SMO (Sweden)
Corrosion Resistance	PRE [1]	51	47.3	47.9	48.1	47.5	46.5
	CPT [2] (℃)	70 - 90	60- 72	70 - 85	68 - 72	65 - 75	55 - 60
	CCT [3] (℃)	50- 70	35 - 55	38 - 48	30 - 40	30 - 35	33 - 43
	corrosion resistance order	SR-50A 〉 UR B26, AL-6XN, 1925hMo, 25-6MO 〉 254SMO					
Mechanical property	UTS (MPa)	min 680	min 650	min 650	min 650	min 650	min 650
	YS (MPa)	min 340	min 320	min 320	min 300	min 320	min 300
	El (%)	min 40	min 40	min 40	min 40	min 40	min 35

* 1) PRE (Pitting Resistance Equivalent) = %Cr + 3.3×%Mo + 30×%N

2) CPT (Critical Pitting Temperature) : 6% Ferric Chloride (FeCl3) Solution

3) CCT (Critical Crevice Temperature) : 6% Ferric Chloride (FeCl3) Sloution

Table 3. Comparison with other super duplex stainless steels

		SR-6DX (Korea)	UR 52N+ (France)	SAF 2507 (Sweden)	UR 45N (France)	SAF 2205 (Sweden)
Corrosion resistance	PRE [1)]	51.9	44.4	45.9	36	36.4
	CPT [2)] (℃)	90 - 95	40 - 70	80 Max.	25 - 40	30 Max.
	CCT [3)] (℃)	50- 60	35 -55	50 Max.	17 - 30	17 Max.
	Corrosion resistance order	SR-6DX > SAF 2507, UR-52N+ > SAF 2205, UR-45N				
Mechanical property	UTS (MPa)	min 820	min 770	min 800	min 680	min 680
	YS (MPa)	min 570	min 550	min 550	min 460	min 460
	El (%)	min 25	min 25	min 25	min 25	min 25

* 1) PRE (Pitting Resistance Equivalent) = %Cr + 3.3×%Mo + 30×%N
2) CPT (Critical Pitting Temperature) : 6% Ferric Chloride ($FeCl_3$) Solution
3) CCT (Critical Crevice Temperature) : 6% Ferric Chloride ($FeCl_3$) Solution

be over 40), however, due to synergistic effect produced by the addition of N and Mo strengthening passive film, it has corrosion resistance characteristic superior to High Cr casting irom, Monel, and Type 420J martensite stainless steel in sea-water, HCl, or Cl- environment. Also this economical stainless steel has strength similar to High Cr casting iron and Type 420J, and corrosion resistance equivalent to Type 316L austenite stainless steel.

This stainless steel is lath-type martensite and therefore has high hardness and good machinability. In order to obtain lath-type martensite, the concentration of austenite-stabilizing elements N, C, Ni, Mn, etc and ferrite-stabilizing elements Cr, Mo, Si, V, etc must be balanced appropriately, and the martensite transformation temperature, Ms, should be higher than room temperature. If ferrite-stabilizing elements are in greater concentration than desired relative to austenite-stabilizing elements, then ferrite phase is formed and hardness, strength, and corrosion resistance is lessened. Likewise when the austenite-stabilizing elements are present at concentrations greater than desired, then residual austenite phase is formed, thereby lessening the machinability. And even when the two groups of stabilizing elements are in good balance, if their total is above desired level, then the martensite transformation temperature drops and in turn the martensite formation suppressed. Therefore, the addition of the stabilizing elements must be controlled. Accordingly, lath-type SR-3MO is created with an optimum balance of the stabilizing elements and at Ms temperature higher than room temperature.

When the pitting corrosion resistance of SR-3MO is compared with other commercial alloys, the following result is obtained in Cl^- environments.

316L A.S.S. 〉 SR-3MO M.S.S. ≥ 304L A.S.S. > 420J M.S.S. > High Cr casting iron

If we want to compare erosion corrosion resistance of SR-3MO with other grades, the application for FGD(Flue Gas Desulfurization) would be the best example for the purpose.

Slurry system of FGD systems requires both good corrosion wear resistance and corrosion resistance. While 304L and 316L A.S.S. display good corrosion resistance, corrosion wear resistance suffers due to poor hardness. High Cr casting iron has high hardness resulting in good corrosion wear resistance, however has poor corrosion resistance characteristic. SR-3MO, having much superior corrosion resistance than High Cr casting iron, while matching its good strength, and superior corrosion resistance than 304L A.S.S. while having 2.5 times its strength, is a supreme match for environments that require both good corrosion wear resistance and corrosion resistance.

Table 4 compares the chemical composition, corrosion parameters, and mechnical properties for FGD alloys.

3. The next-generation duplex stainless steel

As mentioned in section (C) of the previous chapter, duplex stainless steel displays superior tensile and yield strength with less amount of Ni.

From the previous research work, duplex grades may show very high corrosion resistance. Therefore, when their high corrosion resistance is combined with high strength,

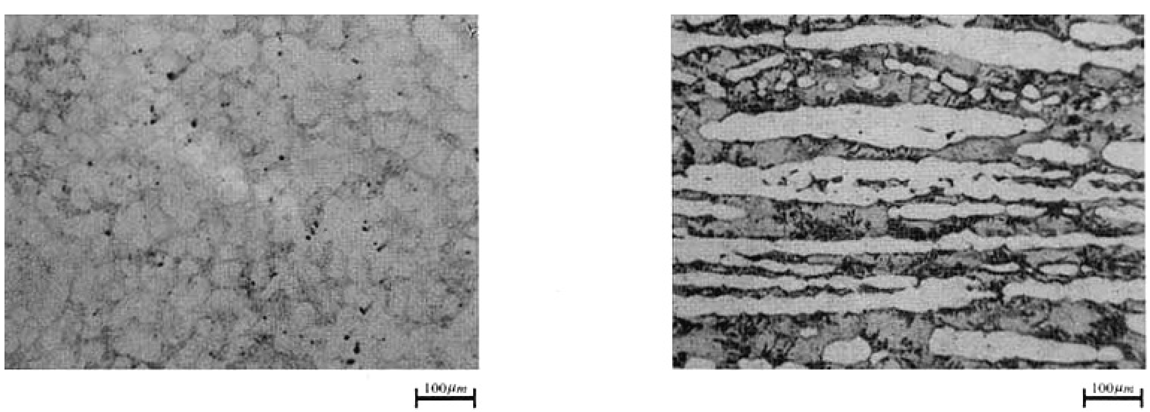
Table 4. Comparison of various metallic materials used in Seawater, wastewater, and sewage treatment plants.

		SR-3MO	420J (CA-40)	High Cr casting iron (A49)	304L (CF-3)	316L (CF-3M)
Chemical composition (wt.%)		Fe+14Cr+ 3.0Mo+0.1N+ 0.3C+1.5Ni	Fe+13Cr+ 0.2 - 0.4C + <1.0Ni	Fe+27.7Cr+ 1.8Mo+1.5C+ 2.6Ni+2.04Cu	Fe+19Cr+ 10Ni+0.03C	Fe+19Cr+ 12Ni+2.5Mo+ 0.03C
Corrosion resistance	PRE (1)	26.9	13	33.6	19	27.3
	Pitting potential (2) (mV vs SCE)	230	80	-200	180	300
	Pitting potential (3) (mV vs SCE)	-60	-	-350	-	-
	Pitting potential (4) (mV vs SCE)	-70	-	-300	-	-
	Corrosion rate (5) (MPY)	2	-	27	-	-
	Corrosion rate (6) (MPY)	3	-	84	-	-
	Corrosion resistance order	316L > SR-3MO > 304L > 420J > high Cr casting iron				
Mechanical property	UTS (Kg/mm^2)	152.5	105.4	-	54.1	56.3
	El (%)	6.6	10	-	60	55
	Hardness (H_{RC})	43	33	46	0.7	0.8
	Mechanical property order	SR-3MO ≒ High Cr casting iron > 420J > 316L ≒ 304L				

*(1) PRE = %Cr + 3.3 x %Mo + 30 x %N
(2) 35°C, 3.5wt % NaCl
(3) 70°C, $H_2SO_4+Cl^-$ (pH : 3, Cl^- : 30,000 ppm)
(4) 70°C, $H_2SO_4+Cl^-$ (pH : 2, Cl^- : 30,000 ppm)
(5) 70°C, $H_2SO_4+Cl^-$ (pH : 3, Cl^- : 60,000 ppm)
(6) 70°C, H_2SO_4 + Cl^- (pH : 2, Cl^- : 30,000 ppm)

the duplex grades will be favored over austenitic grades for construction materials. However, it is well known the duplex grades are susceptible to brittle secondary phase (such as sigma and kai phases) formation. At Yonsei University, a new approach to reduce the forming rate of the secondary phases has been made.

Elements(REM and others) with larger atomic radius (>1.8Å) than those of Cr, Mo and W have been added with B into the duplex steels. The subject steels showed much reduced amount of sigma and kai phases at 650~1,000°C. In addition, fine REM oxides/oxy-sulfides seemed to enhance the retardation effects, refining the phases and grains. Figure 6 shows the microstructures for subject alloys and a commercial super duplex grades(SAF 2507).



(a) (b)

Fig. 6. Microstructures for (a) subject alloys and (b) a commercial super duplex grades (SAF2507)

4. Conclusion

Stainless steels used in seawater facility, water treatment plants, FGD systems and acid resistance systems face constraints in its utilization because of crevice corrosion, pitting corrosion, stress corrosion cracking, hydrogen embrittlement, intergranular corrosion, erosion corrosion, among other problems. To overcome these corrosion problems, and providing with good mechnical property, life times vs. cost advantage, industrial safety, and reliability, SR-50A, a super austenitic stainless steel, and SR-3MO, a martensitic stainless steels with high corrosion resistance are being used extensively as materials for hot coil, castings, strip coil for welded tube, etc. In addition these stainless steels are widely expected to find its application in future platform-seawater system, etc.

In addition, due to its superior corrosion resistance and mechanical property, super duplex stainless steels with suppressed formation of sigma and kai phases are expected to be more widely utilized as raw materials for equipments that either need to handle big volumes of corrosive fluids such as seawater, or heavy-load bearing equipments.

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