

High Nitrogen-Bearing Austenitic Stainless Steels Resistant to Marine Corrosion

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High nitrogen-bearing stainless steel (HNS) containing more than 1mass% N was successfully created by means of pressurized electro-slag remelting (P-ESR) without the addition of manganese. Excellent localized corrosion resistant properties of the HNS were confirmed in terms of pitting and crevice corrosion in artificial seawater. The repassivation kinetics proved higher repassivation rate for HNS.

Keywords : high nitrogen steel, stainless steel, pitting corrosion, crevice corrosion, marine corrosion

1. Introduction

A project called STX-21 launched in 1997 at National Institute for Materials Research (NIMS), of which target is to create innovative structural steels for the next century. One of the topics is "Development of steels for structures in marine and offshore environments". The objective of this research is to develop a resource-saving austenitic stainless steels with highly resistant seawater corrosion. Two key techniques were adopted for this approach; 1) to enhance the cleanliness of metal structure, 2) to add nitrogen as interstitial element in austenitic matrix. Research.¹⁾ High N austenitic steel may be possible by increased addition of Mn but at the expense of corrosion resistance.^{2,3,4)} In the present study, high N addition was attained by melting under a pressurized condition. The properties of pitting and crevice corrosion of new high N steels were investigated in artificial seawater.

2. Experimental

The major specifications of the P-ESR, shown in Table 1, were as follows: maximum weight of ingot: 20 kg in Fe-base; maximum pressure of nitrogen gas: 5 MPa. Fig. 1 shows the schematic diagram of P-ESR, whose pressure

Fig. 1. Schematic diagram of P-ESR.

vessel of 50L in inner volume contains an electrode and copper crucible. Melting tests for the P-ESR were conducted under the conditions of 1, 2, 3 and 4 MPa in nitrogen gas pressure, AC current of 2000~3000 A, voltage of 27~30 V and melting rate of 0.5~0.7 kg/min.

The first primary electrode used for P-ESR was Type 316L stainless steel with very low inclusions. FeCrN powder was used as the nitrogen source, it was packed in stainless steel pipes, sintered, and then spot-welded on the surface of the electrode. Flux used in the tests was a mixture of CaF_2 , CaO and Al_2O_3 , all of which were added into the crucible before the melting test.

3. Results and Discussions

3.1 Nitrogen profile in ingots

An example of a nitrogen profile of an ingot obtained at $P_{\text{N}_2} = 4$ MPa is shown in Fig. 2. Nitrogen was uniformly distributed both in radial and axial directions. It was also found that the nitrogen concentration was 0.7 mass% at $P_{\text{N}_2} = 1$ MPa, 0.9 mass% at 2 MPa, 1.0 mass% at 3 MPa and 1.1 mass% at 4 MPa. It was empirically confirmed that the relation between nitrogen content and pressure could be predicted by using Sievert's law even at high N content.

Composition and phase high N steels (HNS) prepared by PESR are listed in Table 2. In the early trials, N was added to 316L based steels. High-N 316L, however required very higher solution treatment temperature, e.g. 1350C. For 316L type steels, ordinary solution treatment temperature of about 1200 C caused precipitation of Cr_2N at grain boundaries, which resulted in deterioration of

corrosion resistance. To attain Cr_2N free and austenitic structure (γ -phase) at 1200C treatment, 23Cr-based material had a greater advantage. For example a composition of 23Cr-2Mo-1.5N has created a γ -single phase structure as shown in Fig. 3. The trend of γ -phase formation increased with increase in N. Typical composition and phase are summarized in Table 2. It is noteworthy that γ -single phase stainless steel can be created without the addition of Ni or Mn.

3.2 Feature of HNS ingots and hot rolled working

Observation of the macroscopic structure of the ingots showed that they had a solidified columnar crystal structure. No flaws were detected on either the ingot-urface or cross section surface by penetration test. Optical microscopic observation revealed a number of inclusions, all of which were less than 10 micrometer in diameter.

EPMA analysis revealed that the major constituent is Al_2O_3 , partly surrounded by Al-Cr-O inclusions. The reason for the existence of Al-Cr-O inclusions might have been due to the lower Al content compared to the oxygen content.

Hot rolling of the new high N stainless steels was carried out under the conditions of 1240 C x 2 h + reheat of 1240 C x 30 min followed by solution treatment at

1350 C x 30 min-WQ. The final thickness of the hot-rolled plates was 7 mm. The rolling reduction of HNS of more than 1mass% in nitrogen should be in the range of 5%-10% in order to avoid edge cracking of the rolled plate.

3.3 Mechanical Properties of Austenitic HNS

The new HNS showed excellent mechanical properties. Fig. 4 shows the tensile strength and elongation of the steels. The tensile strength increased with increasing N content. The elongation of HNS is of the same level as that of 304 steels and is higher for γ -single structure than $\alpha + \gamma$ structure. The temperature dependence of tensile strength and 0.2 % Proof strength of 23Cr-4Ni-1N steel is shown Fig. 5. The fully austenitic steel showed high strength in wide temperature range of -100 to 600C.

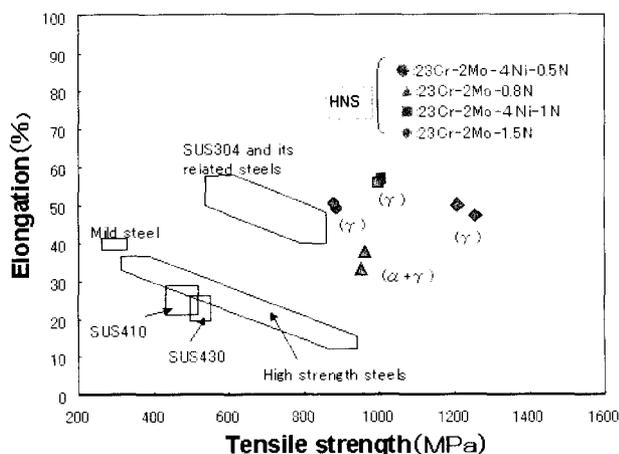


Fig. 4. Mechanical properties of new high-N steels (HNS) as parameters of tensile strength and elongation. New HNSs show high tensile strength yet are as ductile as conventional 304 steels.

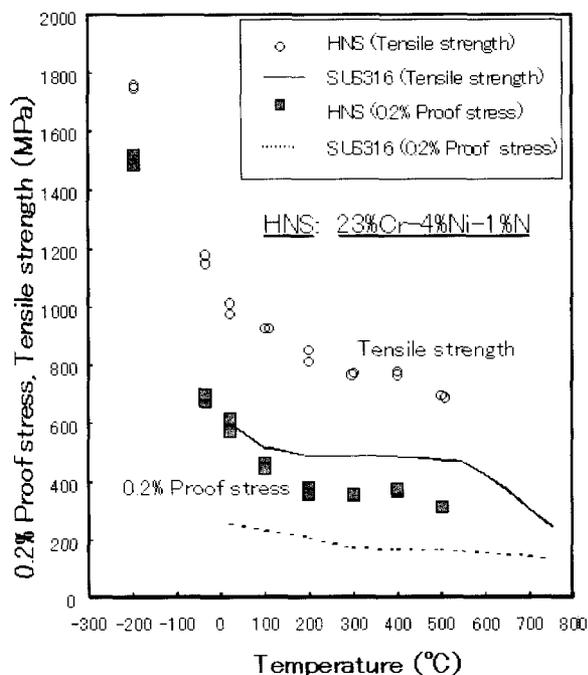


Fig. 4. Temperature dependence of mechanical properties of HNS.

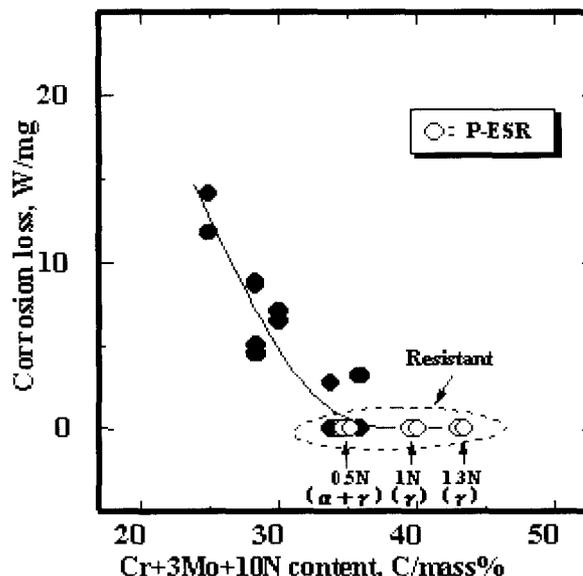


Fig. 5. Corrosion loss of HNS as a function of crevice corrosion equivalence (CCE: Cr+3Mo+10N) in artificial seawater + H_2O_2 generating enzyme environment. The mass loss for low CCE samples is due to the generation of crevice corrosion.

3.4 Crevice Corrosion Test of HNS

The crevice corrosion resistance was evaluated using multi-crevice device in accordance with ASTM G78. Crevice corrosion resistance was evaluated in artificial seawater both by spontaneous immersion or under potentiostatic controlled condition. In the former case relatively noble potential was maintained by adding H_2O_2 generating enzyme system (1mg/L GOD (glucose oxydase) and 10 mg/L glucose). Fig. 5 shows the corrosion loss in crevice corrosion environment plotted as a function

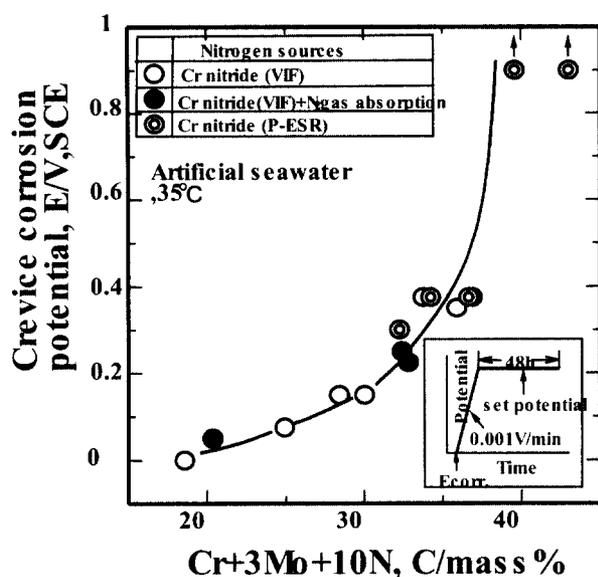


Fig. 6. Crevice corrosion potential of 17/25Cr- 0/14Ni- 2/6 Mo 0.2/1.3 N stainless steels in artificial seawater.

of crevice corrosion equivalence (CCE: Cr+3Mo+10N). Samples produced by PESR are marked by open circles whereas those prepared by conventional vacuum melting are plotted by closed circles. All PESR samples showed null corrosion loss indicating that crevice corrosion did not occur despite high potential (around 0.4 V vs. SCE) due to the presence of H₂O₂. The results indicate that high nitrogen austenitic stainless steels are immune to crevice corrosion in synthetic seawater.

Crevice corrosion potentials were determined by keeping a sample at predetermined potentials for 48 hrs. by means of a potentiostat, followed by anodic current monitoring and visual check. The results of crevice corrosion of HNS obtained in artificial seawater at 35 C are shown in Fig. 6. Crevice corrosion potential was higher than 0.9 V_{SCE} for samples with CCE>38 obtained by P-ESR, meaning that new HNS samples are immune to crevice corrosion even at potentials of oxygen evolution. Pitting potential determination based on JIS G0577 has proven that all these new HNS stainless steels are immune to pitting corrosion in artificial seawater resistance of HNS was evaluated by up to the oxygen evolution.

3.5 Repassivation Kinetics

Static electrochemical corrosion tests clearly showed that high nitrogen steels are very resistant to localized corrosion in seawater. The role of nitrogen for the improved resistance yet enigmatic. For this resolution we measured repassivation kinetics using a scratch electrode as shown in Fig. 7. Stainless steel plate (electrode) placed

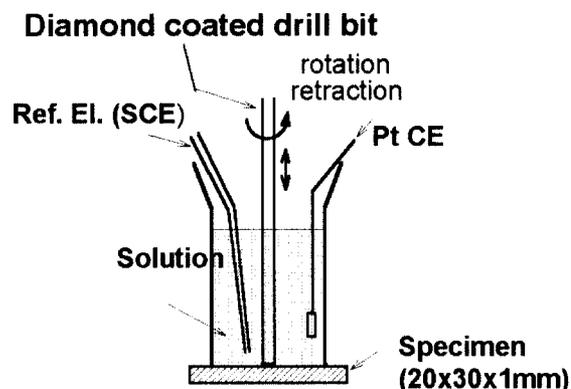


Fig. 7. Device for the measurement of repassivation kinetics.

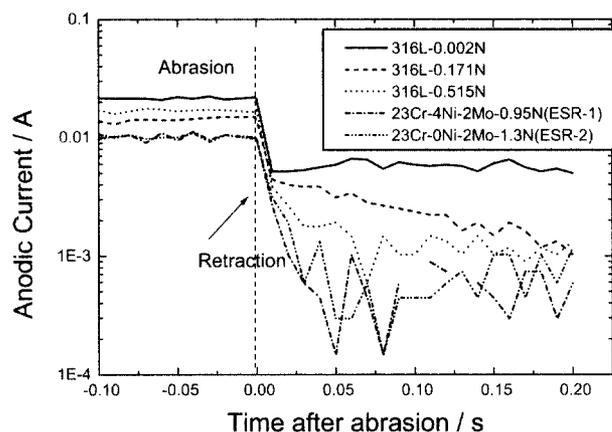


Fig. 8. Current decay following surface scratch of N-bearing SS in 3.5% MN under potentiostatic condition of 0.5V vs. SCE.

horizontally was abraded with a rotating drill bit, the surface of which is coated with diamond. Following the abrasion for about 20 ms the rotating drill bit was abruptly retracted so that passive film is allowed to recover (repassivate). The repassivation process was monitored by the anodic current change on a potentiostat.

Fig. 8 shows anodic current decay following abrasion at a potential of 0.5 V vs. SCE in a 3.5% NaCl solution. In current decay curves are plotted in semi-logarithmic scale. Among five samples tested, three are 316L based stainless steels. 316L samples showed steeper current decay indicating faster repassivation with increasing N content. For PESR samples (23Cr steels) current decay terminated within 50 ms followed by the current fluctuation. Seemingly, interstitial N plays the role of a passivator in corrosion reaction..

3.6 Nitrogen Reaction

It is obviously demonstrated that interstitial nitrogen in

Table 3. Conversion of N in SS to ammonia as the result of electrochemical dissolution of stainless steels.

Steel type (N % in steel)	E V vs.SCE	CC ^{*)}	time hr	NH ₃ -N ppm	NO ₃ -N ppm	NH ₃ conv ^{**)} %
F8 (0.39N)	0.05	-	3	0	0	-
	0.1	+	3	0.15	0.04	102
F4 (0.17N)	0.3	-	6	0	0	-
	0.4	+	6	0.71	0.03	116
F4N (0.52N)	0.4	-	24	0	0	-
	0.7	+	6	1.61	0.03	120

*) CC: +: crevice corrosion occurred, -:no crevice corrosion occurred.

**) Conversion efficiency of interstitial N in SS to ammonia (molar ratio)

stainless steels is effective in repassivation process rather than the enhancement of protectiveness of passive film. The next concern is how it works in the repassivation process. For this purpose nitrogen analysis was carried out for compounds most probably produced in the process of dissolution of N-bearing stainless steels.

Table 3 shows the conversion of interstitial N in steels to dissolved ammonia as the result of electrochemical crevice corrosion in NaCl solution. Most of interstitial nitrogen is converted to NH₃ regardless of electrolysis potential. Nitrite nitrogen was below detectable level in all cases. The conversion of interstitial N to ammonia is cathodic reaction whereas the major reaction is metallic dissolution under impressed anodic current:



In interstitial state nitrogen atom has a lone pair thus it should be far more active than gaseous nitrogen. Since Eq. (1) is a proton consuming reaction, it is, thus, in favor of repassivation at such occluded sites as crevices and pits.

5. Conclusions

1. A new pressurized-ESR furnace has been developed at NRIM, whose maximum nitrogen pressure is 5 MPa,

and maximum weight of ingot is 20 kg in Fe equivalent.

2. By using the P-ESR, high nitrogen-bearing austenitic stainless steel with more than 1mass% of nitrogen was successfully fabricated without the addition of manganese at higher pressure than 3 MPa in nitrogen gas. The distribution of nitrogen in ingots was even under each nitrogen pressure condition.

3. High nitrogen-bearing austenitic stainless steel of 23%Cr-4Ni-2Mo-1.2%N with purity of less than 20 ppm in oxygen content obtained by P-ESR showed excellent localized corrosion resistance, i.e. no crevice corrosion occurred in artificial seawater at 35 C.

4. The pitting corrosion test at 45 C in artificial seawater showed that if the maximum width of precipitates along the grain boundary was less than 1 micrometer, there would be no effect on the pitting potential, while at larger than 10 micrometers pitting potential would be decreased.

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