DEVELOPMENT OF NEW TYPE SEAWATER RESISTANT STEEL AND THE RESEARCH OF ITS STRUCTURE AND CORROSION RESISTANCE

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Abstract

This paper investigated two kinds of corrosion resistant low alloy steels depending on the environment of the North China see (Steel S) and South China sea (Steel N), respectively. The mechanical and corrosion properties of the two steels were analyzed in this paper. Tin was added into both steels to improve the corrosion resistance. Structure and mechanical properties of the two steels were detected, and the results revealed that the microstructures of both steels were ferrite and little divorced pearlite. The yield strength and impact toughness at -40℃ of the steel S are 423MPa and 98 J, respectively. The yield strength and impact toughness at -40℃ of the steel N are 437 MPa and 70 J, respectively. The properties mentioned above met or even exceeded the requirement (yield strength 355 MPa, toughness 34 J) in these areas. The corrosion resistant properties of the two steels were also investigated via the means of immersion test and electrochemical experiment. The immersion test indicated that the corrosion rate of steel S and steel N was 0.00938 mg/h·cm^2 and 0.00838 mg/h·cm^2, respectively, when completely immersed for 168 hours, and the corrosion rate was much lower than that of E36. The Electrochemical experiments showed that the corrosion potential (E_{corr}) of both steels was higher in contrast to E36, which indicated a lower corrosion trend.

Introduction

The development of ocean resource has become a hot topic in recent years, and the development of ocean resource cannot be separated from the infrastructure such as sea oil drilling platforms, seabed pipeline and harbor. So the development of the ocean resource will bring a huge market to the steel industry. The ocean is a complex system filled with salt and creatures [1], so the steel used in ocean engineering has a demand for corrosion resistance except mechanical properties.

The developed countries have developed their own offshore steels such as Mariner steel of America, Aps20A steel of France and Mariloy steel of Japan. Normally, the compositions and microstructures are the main factors that affect the corrosion resistance. The common elements used in corrosion resistant steel are chromium, aluminum, copper and so on. S. Ningshen [2] reported that the corrosion rate of 15% Cr ODS steel after 240 h exposure was much lower than the 12% Cr ODS steel after 48 h exposure. Besides, Lakatos-varsányi [3] got a conclusion that there was a depletion of Cr in the metallic substrate as compared with the bulk material and this process could be explained by a dissolution of Fe and a preferential leaching of Cr leaving behind a thin layer of Fe depleted in its Cr content, and somehow enriched in residual elements. Previous research [4] has reported that the improved corrosion resistance of the Cu containing steel was attributed to the high hydrogen overpotential suppressing the cathodic hydrogen evolution reaction. Generally speaking, the effect of alloy elements on corrosion resistance is that:

(1) the modification of the steel on its rust layer; (2) the improvement of substrate steel's potential.

Besides, in recent years, the ferrite stainless steels has been widely used in automobile industry, kitchen appliances and manufacturing industries due to its relatively higher thermal conductivity, lower thermal expansion, excellent oxidation, corrosion resistance, and lower cost[5]. The combination of excellent property and low cost make ferrite stainless steels more attractive in various industrial. In this paper, we conducted two type of seawater corrosion resistant steel. The microstructures, yield strength and impact toughness (-40℃) of the two steels were investigated to evaluated its mechanical properties.

Experimental

All the specimens were cut from industrial plates processed by TMCP with the thickness of 20 mm. The steel used in the South China sea and the North China sea were marked as Steel S and Steel N, respectively. The compositions of the two new steels and E36 grade are listed in Table 1. The tensile and charpy V-notch impact specimens were cut from the as-rolled plates in the transverse direction. Impact tests were carried out at the temperature of −40 ℃. The specimens for optical microscopy observation were carefully prepared according to the conventional process.

The corrosion tests were conducted under the imitated seawater, the compositions of the solution are shown in the Table 2. Wet-dry cycle corrosion test, submerged corrosion test and salt spray corrosion test were conducted to calculated corrosion rates, respectively, and the weight loss methods were used in this part. All the specimens for corrosion test were cut to the size of 60 mm×30 mm×5 mm, and all specimens were grinded with 400–1200 grit silicon carbide paper.

Table 1 Chemical compositions of specimens (wt.%)

Specimen	C	Si	Mn	P	S	Sn	Cu	Cr	Al
E36 steel	≤ 0.15	≤ 0.20	1.200	0.017	0.003	---	0.039	0.050	0.038
Steel S	≤ 0.15	≤ 0.20	0.900	0.010	0.003	≤ 0.05	≤ 0.60	≤ 0.80	---
Steel N	≤ 0.15	≤ 0.20	0.920	0.010	0.003	≤ 0.05	---	≤ 0.80	≤ 0.90

Table 2 Chemical compositions of solutions (g/L)

Standard solution A		Standard solution B	
$MgCl_2 \cdot 6H_2O$	555.57	KCl	69.46
$CaCl_2$	57.94	$NaHCO_3$	20.10
$SrCl_2 \cdot 6H_2O$	2.12	KBr	10.06
		H_3BO_3	2.72
		NaF	0.30

The exposed surface of the specimens for electrochemical measurements was 10 mm ×10 mm, with an area of 1 cm^2. The electrochemical measurements were performed in a standard three electrochemical cells, with a saturated calomel electrode as the reference electrode, a platinum sheet as the auxiliary electrode, and the samples as the working electrode. The parameters of potentiodynamic tests are as follows; the sweeping potential was from −0.25 to 0.25 V versus the OCP, and the scanning rate was 0.3 mV/s. The specimens immersed for 1 and 4 days were tested by the potentiodynamic polarization measurements.

Results and Discussions

Fig. 1 shows the microstructures of the three steels. We can see that the microstructures of the two new steels are ferrite and little pearlite as shown in Fig. 1(a) and (b), a large amount of pearlite appears in E36 ship plate steel (Fig. 1(c)). And the microstructure of E36 steel is ferrite-pearlite. The microstructures of Steel S and Steel N can meet the requirement. The microstructure of the steel N in Fig. 1(b) is banded structure, since that the rolling process was proceeded in the two-phase region. Besides, it is obvious that the volume fraction of pearlite in E36 steel is higher than that of the two new steels, which means the two new steels is difficult to be corroded than E36 steel [6]. Research [7] has reported that pearlite has passive effect on the corrosion behavior of steel. The cementite lamellar of pearlite is large. Generally speaking, the cementite lamellar is consider to be cathode, and the ferrite is consider to be anode [8]. The little content of pearlite in the two new steels can reduce the cathode in the corrosion reactions.

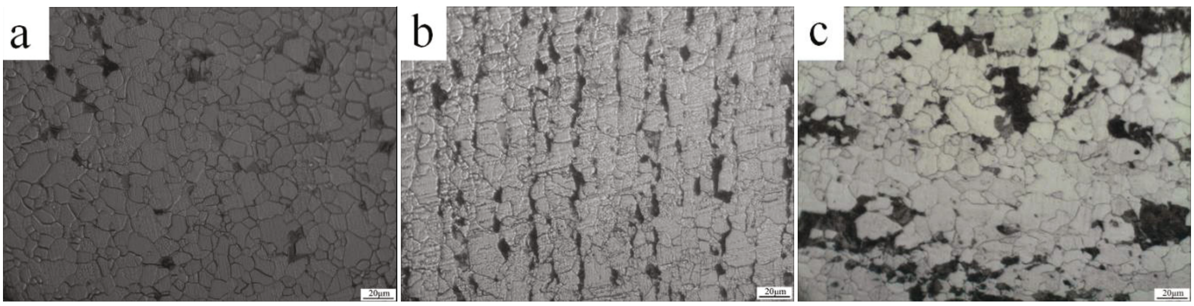

Fig. 1 Microstructures of the three steels. (a) Steel S, (b) Steel N, (c) E36 steel.

Table 3 shows the results of tensile and chart V notch impact tests. The results indicate that both steels met or even exceeded the required property index. Besides, the impact toughness was almost improved by twice compared to required properties, and the elongation of the two steels are also improved. The mechanical tests show that both Steel S and N meet the design requirements of mechanical properties.

Table 3 Results of mechanical test

Steel	Yield strength (MPa)	Tensile strength (MPa)	Elongation (%)	Impact toughness KV_2/J (-40℃)
Steel S	423	506	28	98
Steel N	437	541	26	70
Standard	≧355	490-630	≧22	≧34

Wet-dry cycle corrosion test, submerged corrosion test and salt spray corrosion test were conducted to evaluate the corrosion properties of the two new steels and E36 steel. Weight loss method was used to calculate the corrosion rates, and the corrosion rates were determined by the following expression [9]:

$$\text{Corrosion rate (mg/h·cm}^2) = W/_{S \times T} \tag{1}$$

Where W is weight loss (mg), S is corrosion area (cm^2) and T is corrosion time (h). The immersion testing result was shown in Table 4. We can see the corrosion rates of Steel S and N are lower than that of E36 steel. The lower corrosion rates of two new steels show that the corrosion resistance of both two steels is better than that of E36 steel. The addition of corrosion resistant elements such as Aluminum, chromium and copper should be responsible for it, and the corrosion resistant elements also could enhance the formation of protective rust layer [10]. Besides, the element tin can also increase the corrosion resistance by improving the performance of the rust layer. Results of corrosion rates showed that salt spray corrosion tests which is proposed to simulate the splash region in the actual corrosion situation was the worst corrosion areas, and the submerged corrosion tests showed the minimum corrosion rates. Under the experimental conditions, oxygen reduction represented the most probable reaction that accounts for the partial cathodic process of the corrosion attack. The expression of oxygen absorption corrosion are as follows [11],

$$(1/_2)O_2 + H_2O + 2e = 2OH^- \tag{2}$$

The corrosion process is determined by the oxygen depolarized reaction, which means that the plenty of O_2 will accelerate the corrosion rates. It may be the reason for the highest corrosion rates in salt spray corrosion tests.

Table 4 Corrosion rates of three steels of 168 h corrosion

Corrosion mode	Steel	Corrosion rate (mg/h·cm^2)
Submerged corrosion	Steel S	0.00938
	Steel N	0.00838
	E36 steel	0.01569
Wet-dry cycle corrosion	Steel S	0.02682
	Steel N	0.01636
	E36 steel	0.03567
Salt spray corrosion	Steel S	0.14755
	Steel N	0.10889
	E36 steel	0.21348

Electrochemical measurements were conducted to analyze the corrosion kinetics. Fig. 2 shows the potentiodynamic polarization curves of the specimens that completely immersed for 1 or 4 days. All specimens for E36 steel, Steel S and Steel N exhibit active corrosion behavior, such that the curves in Fig. 2(a) and (b) show that anodic current density gradually increases with increasing potential. This typical behavior indicates that a passive film is not formed on the specimen surface. Corrosion potential E_{corr} obtained from the polarization curve corresponds to zero current, where the sum of all anodic reactions on the specimen surface is equal to the sum of all cathodic reactions. As can be seen from the curves showed in Fig. 2(a) and (b), the E_{corr} of the Steel S and N are higher than that of E36 steel. The value of E_{corr} is usually used to evaluate the corrosion trend, and steel will be easy to be corroded with a lower E_{corr}. So the two new steels with higher E_{corr} show better corrosion resistance than E36.

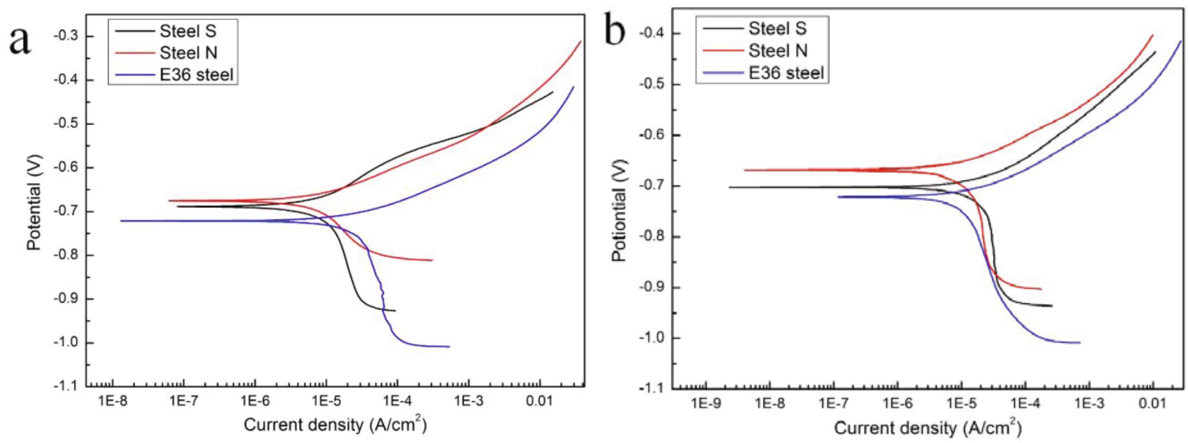

Fig. 2 Potentiodynamic polarization curves of the three steels. (a) immersion for 1 day. (b) immersion for 4 days.

Curves showed in Fig. 2 also reveal that Steel S and Steel N have lower anodic current density compared with tin-free steel at every immersion period. The lower anodic current density means that the anodic reaction on the corrosion surface of Steel S and N is lower than that of E36 Steel, and that means the dissolution of Fe is slow.

Conclusion

1. Microstructures of both Steel S and N were ferrite and little divorced pearlite. The content of pearlite in Steel S and N is lower than that of E36 steel, which means that the two new steels are difficult to be corroded than E36 steel.

2. The yield strength and impact toughness at -40℃ of the Steel S are 423MPa and 98 J, and the values of the Steel N are 437 MPa and 70 J. All of these mechanical properties had already reached or even exceeded the required property index.

3. The corrosion rates of the two steels are much lower than that of E36. Besides, electrochemical measurements show that the Steel S and N have higher E_{corr} than E36, and the higher E_{corr} indicates that the two new steels have lower corrosion trend. Both immersion tests and electrochemical measurements show Steel S and N have better corrosion resistance.

References

1. M S, F T, L E, et al. Corrosion of carbon steel by bacteria from North Sea offshore seawater injection systems: laboratory investigation.[J]. Bioelectrochemistry, 2014, 97(1):76–88.
2. Ningshen S, Sakairi M, Suzuki K, et al. The corrosion resistance and passive film compositions of 12% Cr and 15% Cr oxide dispersion strengthened steels in nitric acid media[J]. Corrosion Science, 2014, 78(1):322–334.
3. Lakatos-varsányi M, Meisel W. Corrosion studies of a chromium steel in imitated seawater[J]. Journal of Radioanalytical and Nuclear Chemistry, 2002, 251(1):75-85.
4. Hong J H, Lee S H, Kim J G, et al. Corrosion behaviour of copper containing low alloy steels in sulphuric acid[J]. Corrosion Science, 2012, 54(1):174–182.
5. Zhang X, Fan L, Xu Y, et al. Effect of aluminum on microstructure, mechanical properties and pitting corrosion resistance of ultra-pure 429 ferritic stainless steels. Materials & Design, 2015,65 :682–689.
6. Liu W, Zhou Q, Li L, et al. Effect of alloy element on corrosion behavior of the huge crude oil storage tank steel in seawater[J]. Journal of Alloys & Compounds, 2014, 598(12):198-204.
7. Zhang C, Cai D, Liao B, et al. A study on the dual-phase treatment of weathering steel 09CuPCrNi[J]. Materials Letters, 2004, 58(9):1524–1529.
8. Y.T. Zhao, S.W. Yang, C.J. Shang, et al. The mechanical properties and corrosion behaviors of ultra-low carbon microalloying steel[J]. Materials Science and Engineering, 2007,454(455): 695–700.
9. Nam N D, Kim M J, Jang Y W, et al. Effect of tin on the corrosion behavior of low-alloy steel in an acid chloride solution[J]. Corrosion Science, 2010, 52(1):14–20.
10. Ryck I D, Evelien V, Biezen, et al. Study of tin corrosion: the influence of alloying elements[J]. Journal of Cultural Heritage, 2004, 5(2):189-195.
11. Wang R, Luo S, Liu M, et al. Electrochemical corrosion performance of Cr and Al alloy steels using a J55 carbon steel as base alloy[J]. Corrosion Science, 2014, 85(1):270–279.