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PHYSICOCHEMICAL PROBLEMS OF MATERIALS PROTECTION

Investigation of Corrosion Behaviors in Chloride Solutions of G-X 10CrNiMoNb 18-10 Austenitic Stainless Steel Produced by Different Casting Techniques[1]

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Abstract—In this study, corrosion resistance of G-X 10CrNiMoNb 18-10 austenitic stainless steel parts, which had been produced through sand molded casting and centrifugal casting methods, and exposed to two-step heat treatments and cooled in different mediums (water, oil, air and oven), in 3.5% NaCl solution were examined according to weight loss, potentiodynamic polarization and impedance spectroscopy. According to the obtained results, it was found that corrosion rate of G-X 10CrNiMoNb 18-10 austenitic stainless steel, which had been cast through the sand molded casting method, heated up to the 1st stage (1065–1120°C), and then cooled in the air, the lowest.

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1. INTRODUCTION

Stainless steels are widely used due to their resistance to corrosion and high temperatures and they contain chromium. Stainless steels are distinguished from other steels due to their resistance, provided by chromium, to corrosion and oxidation. This chromium content of higher than 12% makes iron alloys more passive especially under severe oxidative conditions [1]. Stainless steels are very prevalently used in industry because they are manufactured easily and have high resistance to heat and corrosion [2–5]. One of the most important disadvantages of stainless steels is that they undergo localized corrosion in chloride solutions. Metals like Mo, Ni, V and Si are added into their compositions to prevent it [5–14]. Effect of molding methods used in steel manufacturing on formation of localized corrosion should also be examined. Effect of casting methods on steel corrosion has not been investigated yet in any study. Stainless steel casting methods are generally classified as resistant to either of corrosion or heat. Sand molded casting is the most frequently used method in manufacturing cast steels due to its applicability to very different parts in size and low molding cost. However, the most significant difficulty, which is encountered during manufacturing cast-steel parts, is the gaps, which are formed as a result of shrinkage of the metal while it is solidifying and cooling. The idea of employing pressure to eliminate these gaps resulted in the centrifugal casting method. G-X 10CrNiMoNb 18-10 austenitic stainless steel was used as the material in this study. Test samples were manufactured by using sand molded casting and centrifugal casting methods, and then, they were cooled in oven, the air, oil, and water. Then, their corrosion behaviors in 3.5% NaCl solution were investigated according to weight loss, potentiodynamic polarization and impedance spectroscopy methods.

2. EXPERIMENTAL

2.1. Material

G-X10CrNiMoNb 18-10 (1.4580 or 316 Nb) materials, which had been produced through two methods as sand molded casting and centrifugal casting methods, were used. This material's standard composition and experimental analysis results according to DIN EN 10088-3 are given in Table 1.

2.2. Heat Treatment

First of all, solution heat treatment is applied to G-X 10CrNiMoNb 18-10 austenitic stainless steels. In this process, parts are heated up to high temperatures and tempered. The aim of the treatment is to dissolve chromium carbides, which cause inter-particle corrosion by depositing on particle borders, in the mixture and to cool them at a rate that they cannot be re-formed. In the 2nd stage, the samples were tempered at 550–650°C to stabilize them. Niobium carbide ion maintains its stability at this temperature. Further-

[1] The article is published in the original.

Table 1. G-X10CrNiMoNb18-10 steel's standard composition and experimental chemical analysis composition according to DIN EN 10088-3

	Chemical Composition (wt %)								
	C	Cr	Ni	Mo	Mn	Nb	Si	P	S
Standard Composition	<0.08	16.5–18.5	11–14	2–2.5	<2.0	>8 × C	<1.0	<0.045	<0.03
Used composition	0.076	17	12	2.19	0.93	0.97	0.67	0.026	0.007

Table 2. Numbering according to the cooling types of parts

Part No	Sand mold casting(S)	Part No	Centrifugal casting (C)
S0	Without heat treatment	C0	Without heat treatment
S1	First stage cooling in oven	C9	First stage cooling in water
S5	First stage cooling in oil	C10	First stage cooling in water
S12	Second stage cooling in water	C11	Second stage cooling in water
S13	First stage cooling in air	C12	Second stage cooling in water

more, maximum resistance to corrosion between particles is ensured because chromium carbide formation is prevented. In the study, G-X10CrNiMoNb 18-10 stainless steel materials, which had been produced through two methods as sand molded casting and centrifugal casting methods, were cooled at four different cooling rates after two-stage heat treatment. At 1st stage of heat treatments, solution heat treatment was conducted for 5 hours at 1065–1120°C and stabilization treatment was conducted at 2nd stage for 2 hour at 550–650°C. The samples were allowed to cool after heat treatments in the air, water, oil and oven. Table 2 shows how the samples are numbered according to the cooling type.

2.3. Electrochemical Method

Electrochemical measurements were performed in a classical three electrodes assembly with as G-X10CrNiMoNb 18-10 stainless steel working electrode, a platinum wire as counter electrode and a saturated calomel electrode (SCE) provided with a luggin capillary as reference electrode. A stainless steel cylindrical rod whose exposed surface is 0.785 cm^2 was inserted in a Teflon tube so that only the flat surface was in contact with solution.

Prior the electrochemical measurements, the WE was abraded with emery papers (grade 320-400-800-1200) washed with distilled water and methanol, dried at room temperature and finally immersed to cell. After immersion of the specimen, a stabilization period of 60 min was needed which proved sufficient for open circuit potential to attain a stable value. The potentiodynamic polarization curves were obtained from –1.0 V to +1.0 V with a scan rate of 5 mV/s. Electrochemical parameters (I_{corr}, E_{corr}, I_{pass}, E_{pp}) were obtained from polarization curves.

Impedance measurements were performed at the open circuit potential, using a computer controlled EIS measurements were carried out on steady state open circuit potential (OCP) disturbed with amplitude of 5 mV a.c Sine Wave at frequencies between 10^5 Hz and 0.1 Hz. Electrochemical measurements were carried out with a Gamry Instrument Potentiostat/Galvonastate/Reference 600. Echem Analyst Software was used for plotting, graphing.

2.4. Weight Loss Method

In determining corrosion rate through the weight loss method, surfaces of plates made of G-X 10 CrNiMoNb 18-10 stainless steels in size of 20 × 50 × 3 mm^3 were cleaned by chemical treatments. The prepared samples were cleaned with, first, CCl_4, and then, rinsed with tap water and distilled water respectively. Then, the samples were allowed to achieve constant weight in an oven at 110°C. Constant weights of the samples were measured and recorded. Then, these samples were dipped into 3.5% NaCl solution. Two samples were taken from each solution at particular times (6 hours, 1, 2, 3, 5, 10, 20, 30 days). The samples were removed from the solution and placed into 5% citric acid solution, whose pH value was adjusted to 4.5 (with concentrated NH_3), for 2 hours. Then, they were rinsed with distilled water and allowed to dry in an oven at 110°C. Then, their weights were measured. In this way, their losses in mass were determined to estimate their corrosion rate. The following equation was employed to calculate corrosion rate:

$$\text{Corrosionrate(mdd)} = \frac{\text{weightloss}}{\text{surfaceareaxtime(day)}}.$$

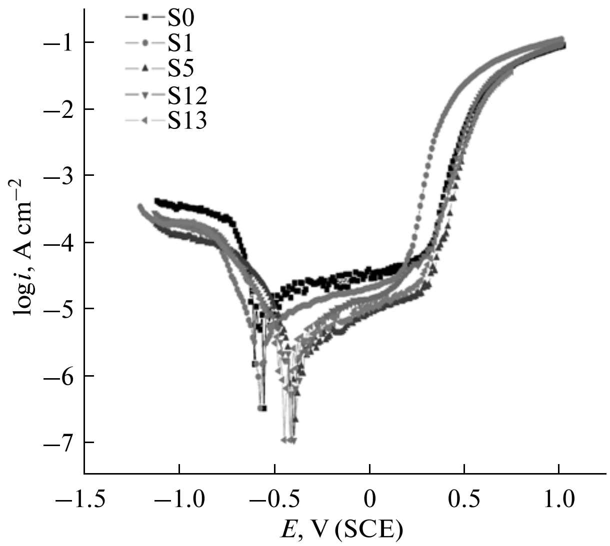

Fig. 1. Potentiodynamic polarization curves of sand molded G-X 10CrNiMoNb 18-10 austenitic stainless steels.

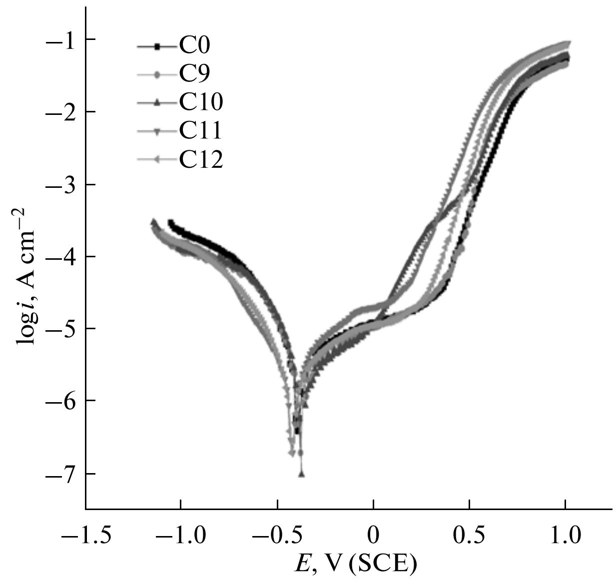

Fig. 2. Potentiodynamic polarization curves of centrifugal casting G-X 10CrNiMoNb 18-10 austenitic stainless steels.

3. RESULTS AND DISCUSSION

3.1. Polarization Results

Figures 1 and 2 show potentiodynamic polarization curves of G-X 10CrNiMoNb 18-10 austenitic stainless steels, which had been produced through sand molded casting and centrifugal casting methods respectively, in 3.5% NaCl solution. As seen in figures, cathodic polarization is within the potential range of approximately −0.50 and −1.2 V. Cathodic reaction in solutions containing 3.5% NaCl is oxygen reduction ($1/2O_2 + H_2O + 2e^- \longrightarrow 2OH^-$). Metal undergoes corrosion at more positive potentials after the corrosion potential. Anodic polarization is within the potential range of −0.58 and 1.0 V. Metal dissolves up to 1st passivation potential, and passive current density decreases compared with the non-heat treated. In other words, heat treatment has caused reduction in passivity current density. Trans-passive zone is entered at 0.12 and 0.35 V. In the trans-passive zone, oxygen release is seen in this zone also due to decomposition of the oxide layer in addition to metal dissolution. Passivation current concentration of potential range of the G-X 10CrNiMoNb 18-10 austenitic stainless steel (S13), which had been heated up to 1st stage (1065–1120°C), and cooled down in the air, is quite lower compared with the sample of S0.

Table 3 shows the electrochemical parameters (i_{corr}, i_{pass}, E_{corr}, E_{pp}) obtained from the potentiodynamic polarization curves. Any significant variation between current densities of heat-treated sand cast and centrifugal cast austenitic stainless steel parts was not observed. This means that casting in different environments did not affect corrosion in stainless steel. However, non-treated C0's corrosion current density was reduced by approximately 3-fold compared with sand cast part (S0). Passivation ends at pit potentials (E_{pp}). It is seen that the smallest pit potential belongs to C10 part because no passivation occurs (Fig. 1). In sand molded casting, passivity current density is highest at S0 and lowest at S13. In centrifugal casting, passivity current density is highest at C11 and lowest at C12. However, a stable passivity is not seen at C10. Corrosion potentials in centrifugal cast parts are higher compared with sand cast parts. Passivity potential range was obtained as wider due to high protective characteristic of the oxide layer formed on surface of the sand cast austenitic steel part.

3.2. Impedance Measurement Results

Figure 3 shows Nyquist curves, which are impedance measurement results of sand cast G-X 10CrNiMoNb 18-10 austenitic stainless steel parts, S0, S1, S5, S12 and S13. In assessment of the impedance results, real *Z* values (Z_{real}) at lower frequencies are important. If a material produces a high Z_{real} value, the surface has good resistance to corrosion. In other words, wider diameters of semicircles in impedance measurements indicate that the material has good resistance to corrosion [16]. An exact semicircle could not be obtained in the Nyquist curves because the material in use had high resistance. As seen according to Nyquist curves also, polarization resistance of the G-X 10CrNiMoNb 18-10 austenitic sand cast stainless steel (S13), which had been heated up to 1st stage (1065–1120°C), and cooled down in the air, is 92.9 kOhm in 3.5% NaCl solution. Considering other sand cast parts, it is seen that this is the best resistance

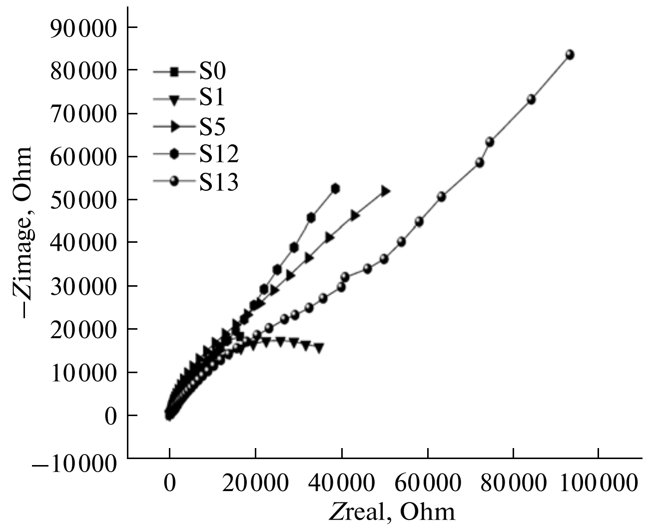

Fig. 3. Nyquist curves of sand molded G-X 10CrNiMoNb 18-10 austenitic stainless steels.

value to corrosion. Polarization resistance of the S5 sample, which had been heated up 1st stage (1065–1120°C), and cooled down in oil, is 49.92 kOhm. Polarization resistance of the G-X 10CrNiMoNb 18-10 austenitic stainless steel (S12), which had been heated up to 2nd stage (550–650°C), and cooled down in water, is approximately 38.50 kOhm. Impedance value of the G-X 10CrNiMoNb 18-10 austenitic stainless steel (S1), which had been heated up to 1st stage (1065–1120°C), and cooled down in oven, is 34.69 kOhm in 3.5% NaCl solution. The part having the lowest polarization resistance among sand cast parts' impedance measurements is non-heat treated G-X 10CrNiMoNb 18-10 austenitic stainless steel part (S0). The value is 16.44 kOhm.

Figure 4 shows Nyquist curves, which are impedance measurement results of centrifugal cast G-X 10CrNiMoNb 18-10 austenitic stainless steel parts (C0, C9, C10, C11, C12). Polarization resistance values of the centrifugal cast G-X 10CrNiMoNb 18-10 austenitic stainless steel part (C10), which had been heated up 1st stage (1065–1120°C), and cooled down in water, and the part (C12), which had been heated up to 2nd stage (550–650°C), and cooled down in water, are quite close to each other 42.84 and 41.80 kOhm respectively. On the other hand, impedance value of the centrifugal cast G-X 10CrNiMoNb 18-10 austenitic stainless steel part (C9), which had been heated up 1st stage (1065–1120°C), and cooled down in water, is 39.53 kOhm. Impedance value of non-heat treated G-X 10CrNiMoNb 18-10 austenitic stainless steel part (C0) in 3.5% NaCl solution is 29.71 kOhm. The part having the lowest polarization resistance among centrifugal cast parts' impedance measurements is the G-X 10CrNiMoNb 18-10 austenitic stainless steel (C11), which had been heated up to 2nd stage (550–650°C), and cooled down in water. The value is 13.50 kOhm. The highest polarization resistance was obtained for S13 among other sand cast and centrifugal cast parts. This result is correlated with the polarization measurement results.

3.3. Weight Loss Results

Figure 5 shows corrosion rate of sand cast G-X 10CrNiMoNb 18-10 austenitic stainless steel changes in 3.5% NaCl solution depending on time. Corrosion rate decreases after tenth day in all parts due to a stable

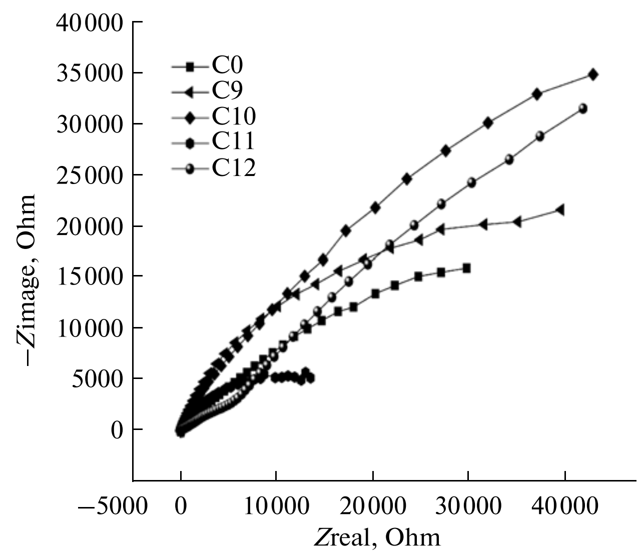

Fig. 4. Nyquist curves of centrifugal casting G-X 10CrNiMoNb 18-10 austenitic stainless steels.

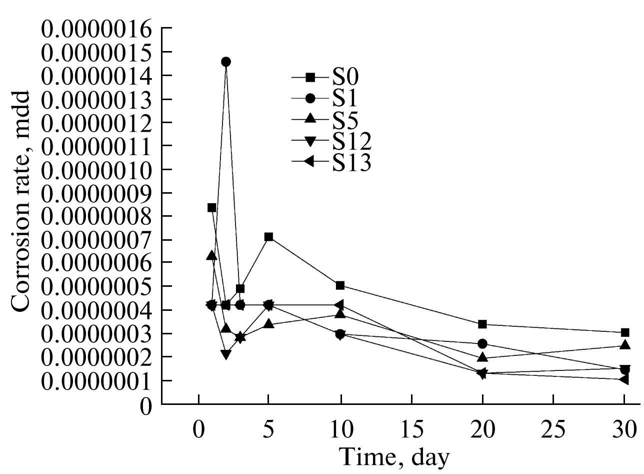

Fig. 5. Variation curve of corrosion rate of sand cast G-X 10CrNiMoNb 18-10 austenitic stainless steel parts versus time.

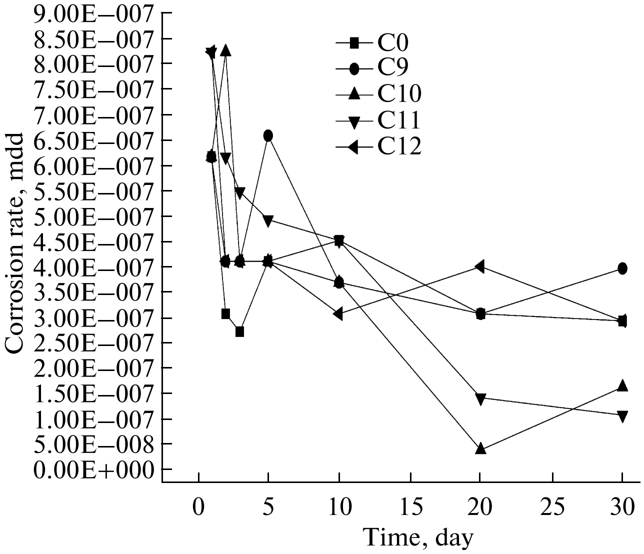

Fig. 6. Variation curve of corrosion rate of centrifugal casting G-X 10CrNiMoNb 18-10 austenitic stainless steel parts versus time.

passive oxide layer formed on the surface. The lowest rate on 30th day occurred in S13 as 9.641×10^{-8} mdd.

Figure 6 shows corrosion rate of centrifugal cast G-X 10CrNiMoNb 18-10 austenitic stainless steel changes in 3.5% NaCl solution depending on time. Because the oxide layer formed on the surface is instable in case of centrifugal cast samples like in case of sand cast parts, corrosion rate varies with oscillations in all parts in the first ten days. After the tenth day, corrosion rate decreases after tenth day in case of centrifugal cast samples due to the tough oxide layer on the surface. The highest decrease occurred in C10 until 25th day and on 30th day, oxide layer on C10 is deteriorated and corrosion rate of C11decreases more.

4. CONCLUSIONS

In the study, sand cast and centrifugal cast G-X 10CrNiMoNb 18-10 austenitic stainless steel materials were treated with heat in two stages (solution heat treatment at 1065–1120°C and stabilization at 550–650°C respectively), and cooled down in various environments (air, water, oil and oven). Then, corrosion behaviors of these samples in 3.5% NaCl solution were investigated through in weight loss, potentiodynamic polarization method and impedance spectroscopy. As a conclusion:

• According to potentiodynamic polarization curves, the highest current density was obtained in non-heat treated S0 and the lowest value was obtained in sand cast S13, which heated up to 1st stage (1065–1120°C) and cooled down in the air among sand cast and centrifugal cast G-X 10CrNiMoNb 18-10 austenitic stainless steels. It was seen that passivity current densities were in correlation with corrosion current densities of centrifugal and sand cast parts. However, a stable passivity is not seen at C10.

• Electrochemical impedance spectroscopy of the G-X 10CrNiMoNb 18-10 austenitic stainless steel parts were investigated in 3.5% NaCl solution. According to Nyquist curves, the highest polarization resistance was produced by S13 and the lowest by C11. This is in correlation with the potentiodynamic polarization results.

• Loss in mass in sand and centrifugal cast parts left in 3.5% NaCl solution was observed to determine their corrosion rate. According to this, the lowest corrosion rate value was produced by S13 and other parts corrosion rates varied within certain ranges.

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