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INFLUENCE OF SIGMA PHASE ON GENERAL CORROSION OF AUSTENITIC STAINLESS STEEL

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ABSTRACT

Austenitic stainless steel is mostly used at high temperatures. It is known that during heating of the austenitic stainless steel with increasing temperature and time of annealing a microstructure is changed i.e. there is the precipitation of carbides followed by precipitation of secondary phases as a sigma phase. The presence of the delta ferrite in austenitic stainless steel enhances the formation of the sigma phase. This study represents the influence of delta ferrite on the sigma phase formation and the effect of the sigma phase on general corrosion. Corrosion tests were conducted in the corrosion cell according to Standard ASTM G5, on instrument potentiostat/galvanostat, Princeton Applied Research, model 263A-2, with the software PowerCORR® (Standard, ASTM G5-94). Examinations were carried out in 1% HCl and 10% $FeCl_3$ solutions. Tafel extrapolation method was used for the investigation of general corrosion. The results of corrosion testing indicated that the intensity of the general corrosion increases with the increase of the delta ferrite and sigma phase contents.

Keywords austenitic stainless steel; general corrosion; delta ferrite; carbides; sigma phase

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1. INTRODUCTION

Austenitic stainless steels are widely used in all industry sectors (transport, food, chemical, building industry, etc.) owing to their good mechanical properties (strength and toughness at elevated and room temperature) and corrosion resistance. The austenitic types of stainless steel have different chemical compositions and properties but the common characteristic is austenite microstructure which is stable at room temperature. Depending on the chemical composition of austenitic steel, it is possible to find the presence of other phases in the austenite matrix called delta ferrite. The alphagenic elements (Cr, Si, Ti, Al, Mo, V, Nb, and W) stabilize and support the formation of the delta ferrite [1-3]. The effects of the delta ferrite on the corrosion resistance of the austenitic stainless steels are not yet clearly understood. However, the effect of the delta ferrite on corrosion resistance of the austenitic stainless steel is usually explained by the formation of Cr depleted zone, low concentrations of Cr and Mo in the austenite phase, precipitation of a sigma phase, and segregation of sulfur or phosphorus along with the δ/γ interface [3-6].

The microstructure of austenitic stainless steel is monophasic ie. austenitic and it is stable at room temperature, but with heating (usually about 500 °C) the microstructure becomes unstable. Since austenitic stainless steels are commonly employed in high-temperature regions, it is important to study the microstructure stability because it influences on properties of these steel, especially mechanical and corrosion properties. During annealing or welding of these steels, the precipitation of the carbides ($M_{23}C_6$, MC, M_6C, and M_7C_3) occurs firstly and is followed by precipitation of other intermetallic phases (σ, χ, η, G, R, and other phases). The presence of the delta ferrite in austenitic stainless steel promotes the precipitation of secondary phases, particularly carbides and sigma phases [7,8].

There are several techniques for testing of corrosion behavior of the austenitic stainless steels in different media, but the electrochemical cyclic polarization technique and potentiodynamic measurements in chloride-containing media are mostly used.

2. MATERIALS AND METHODS

This work aims to investigate the effect of delta ferrite on the formation of the sigma phase and also the effect of the sigma phase on general corrosion. Two types of samples were used for this testing, the sample with 10.38% delta ferrite and a sample with 0.10% delta ferrite. The chemical composition and the delta ferrite content of tested samples are given in Table 1.

Table 1. Chemical composition and the delta ferrite content of tested samples [11]

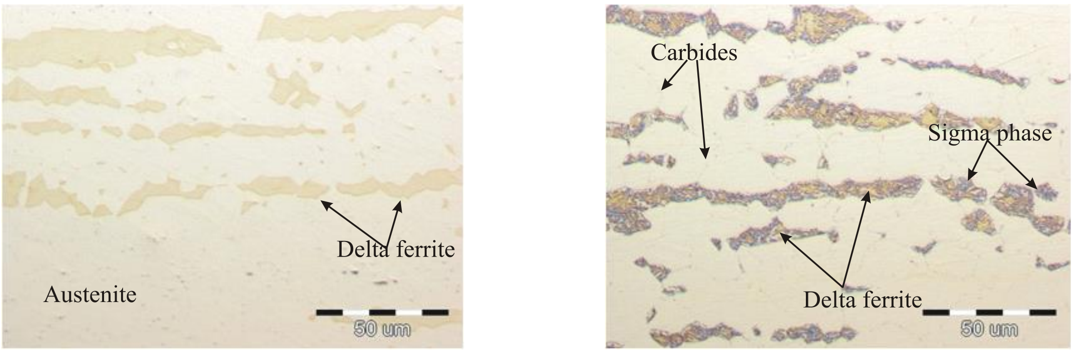
Sample	Chemical composition, wt %								Delta ferrite, %	
	C	Si	Mn	Cr	Ni	N	P	S	Initial state	Annealed at 750 °C
1692	0.04	4.41	7.4	18.0	8.1	0.183	0.007	0.005	10.38	0.94
1720	0.05	3.9	9.0	16.0	8.7	0.179	0.007	0.006	0.10	0.00

According to previous research, increasing the content of delta ferrite increases the rate of sigma phase precipitation during annealing at high temperatures [9-11].

Testing of general corrosion resistance was performed in 1% HCl and 10% $FeCl_3$ solution. Samples were taken from the rod with 10.38% (1692) and 0.10% (1720) delta ferrite and tested in the solution annealed state (1030 °C/60 minutes/water). After that, the solution annealed samples were again annealed at 750 °C for 30 minutes and air-cooled.

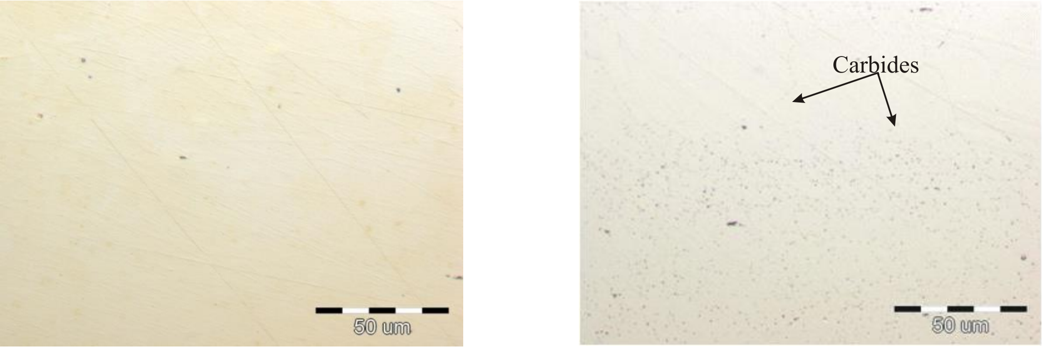
The aim of this annealing was the decomposition of the delta ferrite and precipitation of the sigma phases and carbides

The delta ferrite content was determined using the magnetic induction method by Feritscope MP 30E-S probe EGAB 1.3 Fe. Microstructures of the initial state of samples are presented in Figures 1 and 2. The metallographic examination was performed on Olympus optical microscope with max. magnification of 1000x, but the most representative figures of microstructure were at a magnification of 500x, which is highlighted in this work. Murakami's (10 g $K_3Fe(CN)_6$, 10 g NaOH and 100 mL H_2O) and Kalling's (100 mL HCl, 5 g $CuCl_2$, and 100 mL C_2H_5OH) reagents were used for etching. Murakami's reagent at room temperature was used for the identification of carbides while heated at 100 °C was used for identification of the delta ferrite and sigma phase. Murakami's reagent at high temperature (90-100 °C) colored the delta ferrite in brown and the sigma phase in blue. Kalling's reagent was used for the identification of the delta ferrite. The microstructure of sample 1692 at room temperature is austenitic with the delta ferrite stringers elongated in the rolling direction. After annealing at 750 °C for 30 minutes, delta ferrite, sigma phase, and carbides were present in the austenitic microstructure. From Table 1, it can be seen that the content of delta ferrite decreased after annealing at 750 °C for sample 1692. The delta ferrite decomposed into the carbides, secondary austenite, and sigma phase. The carbides precipitation at the austenitic grain boundary was observed too. The microstructure of the 1720 sample is austenitic at room temperature but the carbides precipitation at the austenitic grain



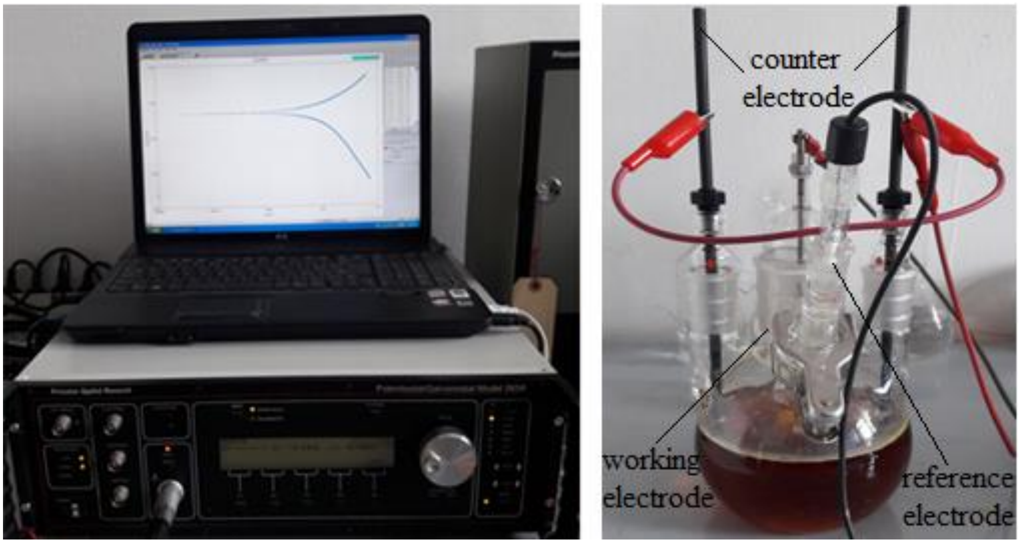
a) b)

Figure 1. Microstructure of sample 1692: a) solution annealed state and b) annealed at 750 °C for 30 minutes, Murakami's reagent, x500 [11]



a) b)

Figure 2. Microstructure of sample 1720: a) solution annealed state and b) annealed at 750 °C for 30 minutes, Murakami's reagent, x500 [11]



a) b)

Figure 3. Representation of the corrosion testing equipment: a) potentiostat/galvanostat, PAR, model 263A-2; b) corrosion cell with electrodes.

boundary after annealing at 750 °C for 30 minutes has occurred. Corrosion tests were carried out in the corrosion cell according to Standard ASTM G5, on instrument potentiostat/galvanostat, Princeton Applied Research, model 263A-2, with the software PowerCORR® (Standard, ASTM G5-94), Figure 3. The investigation was performed in 10%

$FeCl_3$ and 1% HCl solution. Tafel extrapolation method was used for general corrosion examinations. This method implies scanning of working electrode potential on the order of ± 250 mV in relation to its Open Circuit Potential (E_{OCP}), at the speed of 0.2 mVs^{-1}.

Tests were conducted at room temperature, 20±1 °C. A standard three-electrode corrosion cell was used. The working electrode was tested austenitic stainless steel in the form of a disk embedded into a holder and exposed to the area of $A = 113.1\ mm^2$. A saturated calomel electrode (SCE) as the reference electrode with a constant potential (0.2415 V) and two graphite rods as counter electrodes were used. The potential was measured versus the reference electrode.

3. RESULTS AND DISCUSSION

The results of general corrosion tests of investigated austenitic stainless steels are given in Figures 4 and 5 and Table 2. Figures 4 and 5 as well as Table 2 show the values of open circuit potential (E_{OCP}), corrosion current density ($i_{corr.}$), and corrosion rate ($v_{corr.}$) samples of stainless steels treated in solutions of 1% HCI and 10% $FeCl_3$. The corrosion current density is a key factor for rating the corrosion rate while the open circuit potential is a more qualitative indicator of the corrosion process. Sometimes, it could be a general indicator of the corrosion rate.

By the testing of samples in 1% HCl solution, considering that the corrosion current density is proportional to the corrosion rate, the lowest value of current density was noticed for the melt 1720 in an initial state, so its corrosion rate was the lowest (3.712 mm/year).

The open-circuit potential, E_{OCP} (I=0) is qualitatively estimated as corrosion resistance. This melt also has the most positive E_{OCP} value, and thus the highest resistance to general corrosion. Metallographic analysis showed that melt 1720 in the initial state after solution annealing has 0.10% delta ferrite, and after additional annealing, the delta ferrite content is zero, while the presence of carbides was observed.

After treatment in 10% $FeCl_3$ medium, a lower value of current density was also recorded, and thus the corrosion rate for 1720 melt (initial state) in comparison to the same melt in the annealed state.

The highest corrosion rate was detected on the samples of melt 1692 after accomplished heat treatment regimes and treatments in 1% HCI solution and 10% $FeCl_3$ solution, which indicates a higher tendency for general corrosion.

Table 2. The values of open circuit potential, corrosion current density, and corrosion rate

Samples	E_{OCP} (I=0) [mV]	$i_{corr.}$ [µA/cm²]	$v_{corr.}$ [mm/year]
1692p1) 1% HCl	-468.018	$1.625 \cdot 10^3$	$1.888 \cdot 10^1$
1692z2) 1% HCl	-482.183	$1.521 \cdot 10^3$	$1.766 \cdot 10^1$
1720p 1% HCl	-452.303	$3.197 \cdot 10^2$	3.712
1720z 1% HCl	-457.481	$5.014 \cdot 10^2$	5.822
1692p 10% $FeCl_3$	-1.186	$8.320 \cdot 10^3$	$9.662 \cdot 10^1$
1692z 10% $FeCl_3$	-111.54	$1.264 \cdot 10^4$	$1.468 \cdot 10^2$
1720p 10% $FeCl_3$	-33.92	$3.435 \cdot 10^3$	$3.989 \cdot 10^1$
1720z 10% $FeCl_3$	-105.824	$7.408 \cdot 10^3$	$8.603 \cdot 10^1$

1)p-solution annealed state (1030 °C/1 h/water)

2)z-solution annealed state (1030 °C/1 h/water) and annealed state (750 °C/30'/air)

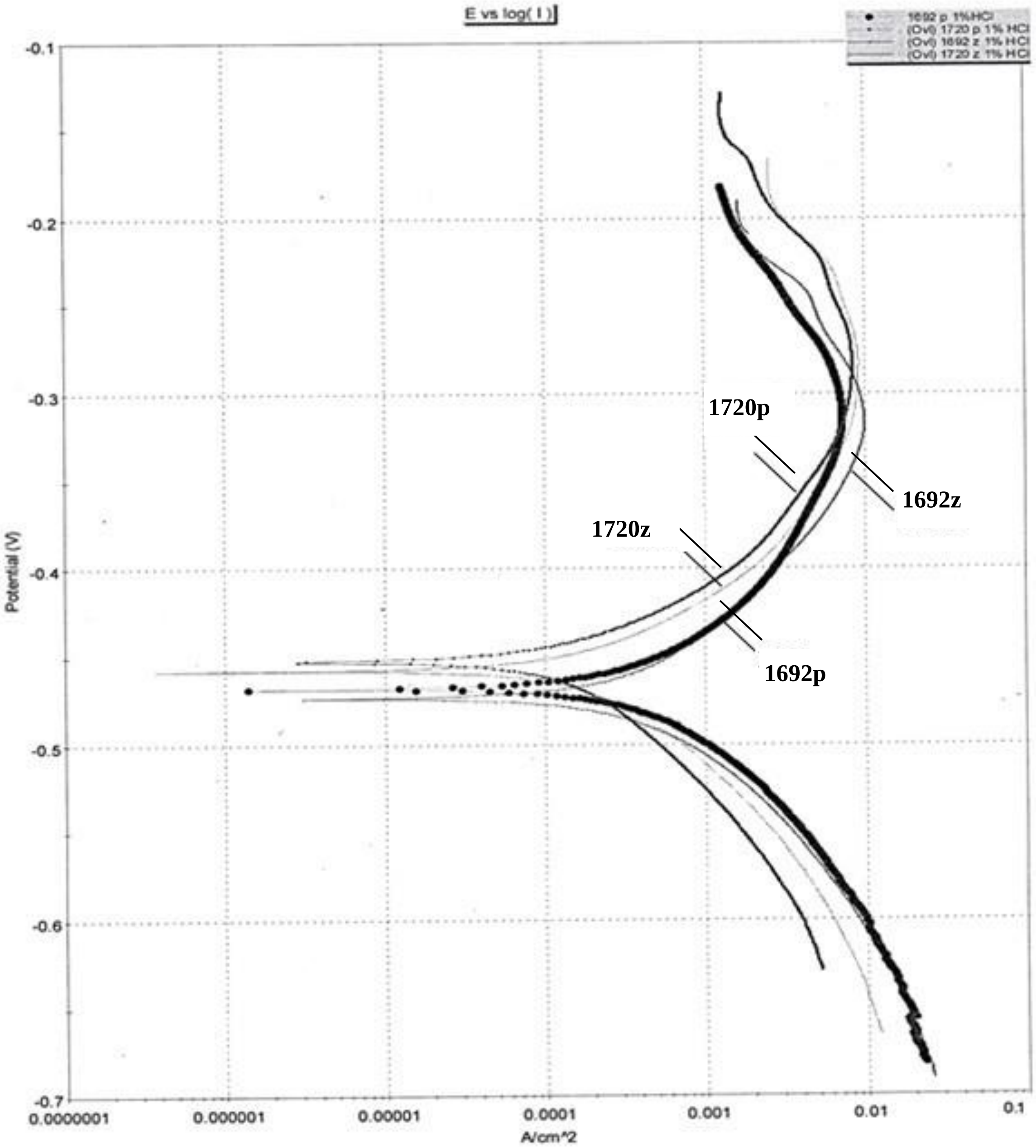


Figure 4. Polarization curves determined by the Tafel extrapolation method after treatment in 1% solution of HCl, 1692 and 1720 melts – initial and annealed state.

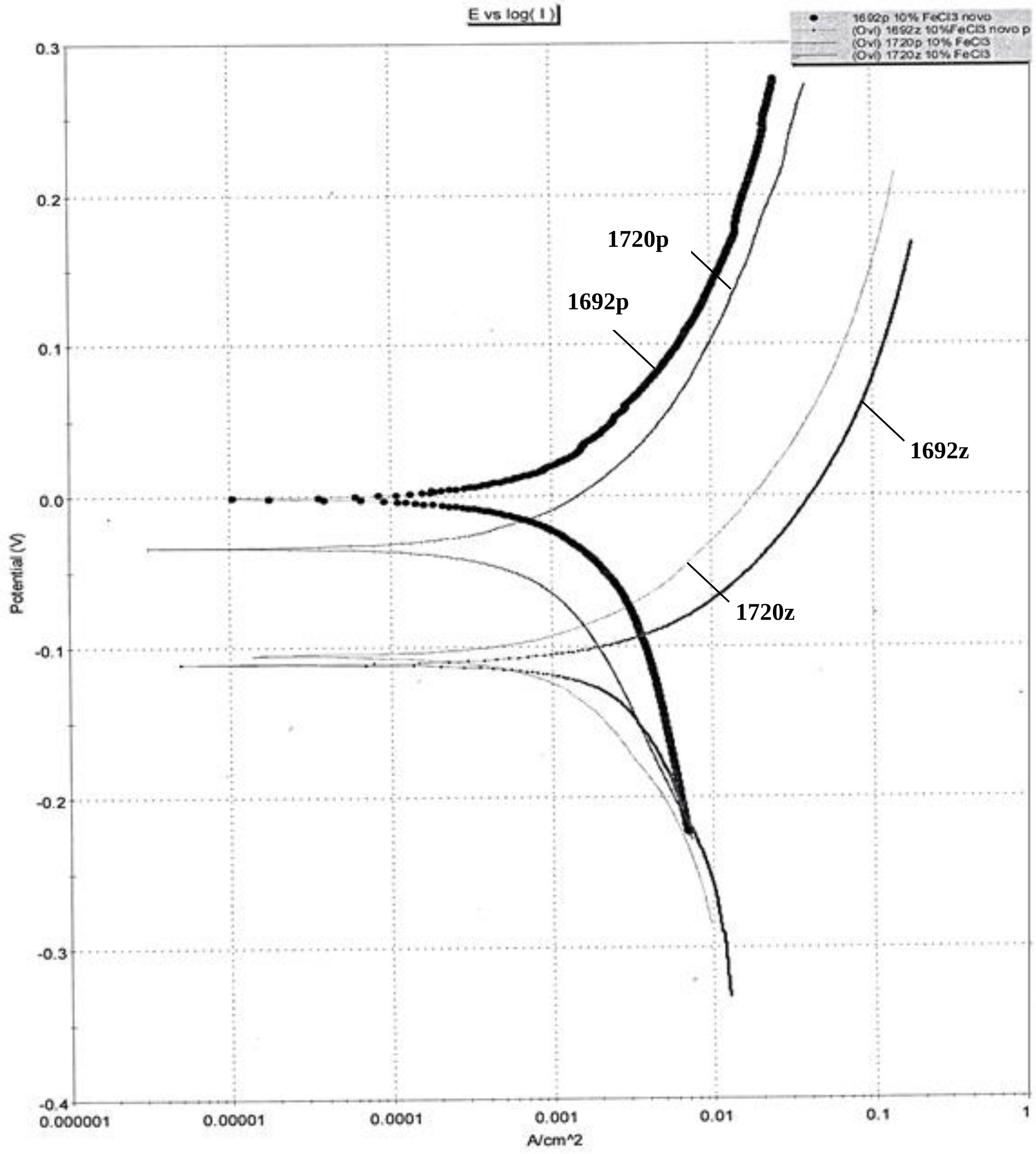


Figure 5. Polarization curves obtained by Tafel extrapolation method after treating in 10% solution of $FeCl_3$, 1692 and 1720 melts – initial and annealed state.

4. CONCLUSIONS

In this work, the influence of delta ferrite on the sigma phase formation as well as the effect of the sigma phase on general corrosion are presented. From the results and analysis, it could be concluded as follows:

- A greater tendency for general corrosion was observed in the samples of melt 1692 with higher content of delta ferrite after performing heat treatment regimes and exposure to appropriate media.
- The melt 1720 with lower delta ferrite content in the initial state as well as without the precipitated sigma phase in the annealed state showed a better corrosion resistance.
- Microstructural changes identified by metallographic analysis after annealing at 750 °C, as well as testing in a very aggressive medium (10% $FeCl_3$), were affected by considerably worse results of the general corrosion resistance tests in the case of melt 1692 compared to the initial, ie. solution annealed state.

Conflicts of Interest

The authors declare no conflict of interest.

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