Effect of ageing heat treatment on corrosion behavior of 17-4 PH stainless steel in 3.5% NaCl

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Abstract

The 17-4PH alloy is a martensitic stainless steel with 3–5 wt% Cu, strengthened by the precipitation hardening. Due to excellent mechanical properties, corrosion resistance and ease of heat treatment, this alloy has unique applications in nuclear power plants and marine constructions. In this paper, the influence of ageing heat treatment, solution annealing followed by ageing at 480, 550 and 620 °C on the corrosion behavior of 17-4PH stainless steel in 3.5% NaCl is reported. Various DC electrochemical measurements and microscopical examination was used. The slow scan rate potentiodynamic polarization revealed that by increasing ageing temperature from 480 to 550 °C, the pitting potential is significantly increased, but further increasing the ageing temperature to 620 °C reduces the pitting potential. Microscopical observation also confirmed the formation of several metastable and stable pits in the sample aged at 620 °C.

Keywords: 17-4PH stainless steel, Corrosion, Ageing heat treatment, Potentiodyanimc polarization.

1. Introduction

Precipitation-hardened stainless steels were first developed during the 1940s, and since then, their application has increased steadily [1,2]. The most important of these properties are easy fabrication, high strength, relatively good ductility, and exceptional corrosion resistance [1-5]. The 17-4PH (AISI Type 630 or UNS S17400) stainless steel from this family is a martensitic stainless steel containing approximately 3-5 wt.% Cu and is strengthened by the precipitation of nano-dispersed copper enriched zones inside the tempered lath martensitic matrix with low carbon content which are stable at room temperature [3-6]. After solution treatment, 17-4PH exhibits a martensitic microstructure but not enough high hardness. Subsequent precipitation ageing treatment in the temperatures between 480 and 620 °C increases hardness and strength [2,4]. The application of this alloy has increased in marine constructions, oil and chemical industries and nuclear power plants due to their excellent combination of mechanical property, corrosion and oxidation resistance comparable to type 304 austenitic stainless steel and type 410 martensitic stainless steel, respectively [8,9]. But, the alloy exposed to seacoast atmosphere will gradually develop overall light rusting and pitting in all heat-treated conditions. It is almost equal to type 304 and much better than the standard hardenable stainless steels in this environment [8-10].

Researches on corrosion behaviour of 17-4PH stainless steel, particularly in chloride environment, are scarce [11-13]. In the present study, the influence of ageing heat treatment on corrosion resistance in 17-4PH stainless steel in 3.5% NaCl solution is investigated by utilizing microscopic studies, determining the pitting parameters by potentiodyanimc polarization measurements, corrosion potential and passivity current.

2. Materials and experimental methods

17-4PH stainless steel bar with 93 mm in diameter and 400 mm in length was used. Chemical composition analysis of alloy (in wt%) is 0.01%C, 0.86%Mn, 0.021%P, 0.007%S, 0.8%Si, 15.74%Cr, 3.96%Ni, 0.06%Mo, 2.74%Cu, 0.3%(Nb+V) and Fe balance, which is in agreement with the ASTM A705 (grade 630) standard for precipitation hardening forged stainless steel [14].

Three different ageing heat treatments, labeled A, B and C, based on ASTM A 705 [14], were performed, as summarized in Table 1, to obtain peak-aged, intermediate and over-aged specimens [15].

For corrosion studies, identical samples with cross-section area of 5×5mm^2 were obtained. Before corrosion tests, the samples were degreased in 10% NaOH for 1 minute at 50-60°C, washed by distilled water and dried. In the next step, the samples were ultrasonically cleaned in acetone for 2 minutes at room temperature. The interface between sample and mounting material was covered by lacquer [16], to avoid the crevice corrosion between the specimen and

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mounting material during the corrosion tests.

Table 1. Summary of ageing treatment on 17-4PH used in this research.

Label	Conditions	Heat treatment
A	H900	Condition A(1h)→480°C×1h→air cool
B	H1025	Condition A(1h)→550°C×4h→air cool
C	H1150	Condition A(1h)→620°C×4h→air cool

An ACM Potentiostat was employed for the electrochemical tests including working electrode, reference electrode and counter electrode. Saturated calomel reference electrode and platinum wire with a surface of 2 cm^2 were chosen as counter electrode. All corrosion tests were performed in a 3.5%wt NaCl solution at ambient temperature. First the rest potential was measured i.e. each sample was placed inside the solution for 3600 seconds and the changes in its corrosion potential were recorded. Each test was repeated 3 times to ensure reproducibility, and average values were reported as rest potential. Potentiodynamic polarization was done with a slow scan rate of 0.05 mV/s in a range of 200 mV cathodic potential, was offset to the rest potential up to the potential value where the sudden current increase was occurred due to extensive pitting corrosion. After anodic polarization close to pitting potential, the samples was ultrasonically cleaned, then they were washed with alcohol and dried. The samples were then etched by Vilella's reagent and stable and metastable pitting morphologies were observed by SEM. Micrographs were taken by an electron microscope LEO 1455VP (SEM) with a 15 kV power.

3. Results and discussion

Variations in OCP of aged specimens of 17-4PH stainless steel immersed in 3.5% NaCl were monitored and the results are presented in Fig. 1. As can be seen, the corrosion potential shows the tendency of passivity characteristics by gradual increasing with time. However, all three samples almost reach the steady state after one hour exposure in 3.5% NaCl. Comparing OCP values reveals that while ageing at 480 °C modifies the OCP to -118 mV; it reduces the OCP to -130 mV by ageing at 620 °C.

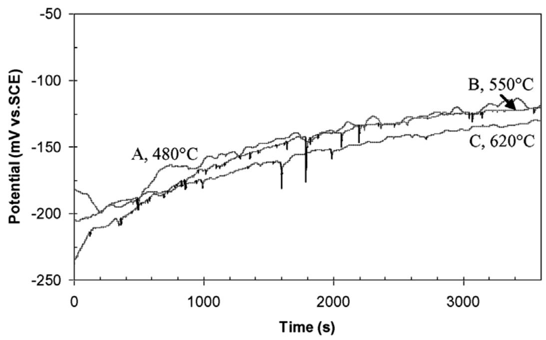

Fig. 1. Variation of OCP for aged specimens of 17-4PH stainless steel immersed for 1 hour in 3.5% NaCl solution.

The slow scan rate potentiodynamic polarization curves for aged samples of 17-4PH stainless steel, A, B and C are shown in Fig. 2. The values of OCP (after one hour immersion time), the pitting potential (E_{pit}) and passivity current (i_{pass}) were obtained and the results were shown in Table 2.

Table 2. The values of OCP (after one hour immersion time), the pitting potential (E_{pit}) and passivity current (i_{pass}).

Condition	OCP(mV)	E_{pit}(mV)	i_{pass}(μA)
A	-118	+173	0.27
B	-120	+205	0.18
C	-130	+124	0.1-0.22

Concerning the pitting resistance, it appears that by increasing ageing temperature from 480 to 550 °C, the pitting potential is significantly raised, but further increasing the ageing temperature up to 620 °C reduces the pitting potential down (Table 2). Therefore, ageing at 550 °C, sample B, results the highest pitting resistance.

The passivity currents in the range of 0.1 to 0.3 μA/cm^2 is obtained for aged samples. By utilizing a very slow scan rate (0.05 mV/s) potentiodynamic polarization, the existence of metastable pits could also be exhibited as the current fluctuations in passivity range (Fig. 2).

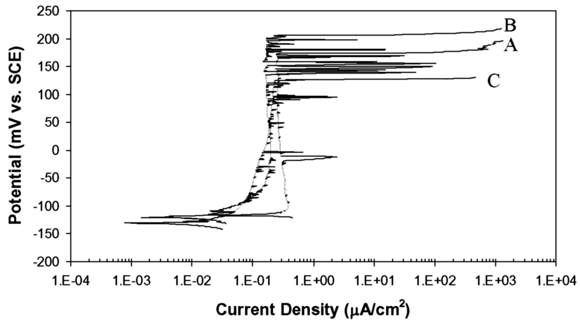

Fig. 2. Potentiodynamic polarization curve for 17-4PH stainless steel in labeled A, B and C, immersed in 3.5% NaCl solution. Scan rate was 0.05 mV/s.

In passivity potential domain, the amplitude of fluctuations is bigger in A (aging in 480°C) and B than the one in C, while the fluctuations frequency (the number of current peaks) is greater in C than that in A and B. This means that the pitting sites in C (aging in 620°C) are much more than those in A and B, but they generate less current compared to the A and B. This subject is also confirmed by Fig. 3.

Passivity current density curves versus time is extracted from potentiodynamic polarization curves (Fig.2), offset to the anodic potential up to the pitting potential, for aged samples of 17-4PH stainless steel, A, B and C are shown in Fig. 3. The irregular current fluctuations observed on curves can be attributed to the formation of metastable pits, which is more enhanced in C. This again confirms the previous potentiodynamic measurements in Fig. 2. The difference in amplitude and frequency of metastable pits can be attributed to the microstructure changes including the volume fraction and the morphology of constituents and precipitates during various ageing heat treatment.

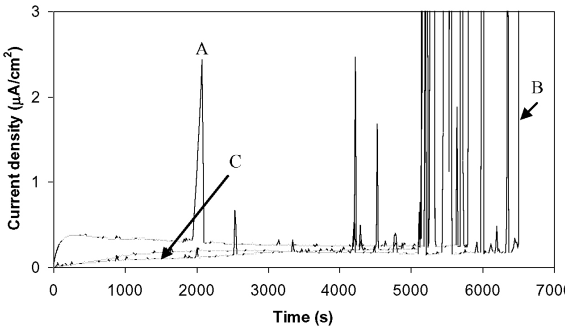

Fig. 3. Passivity current density curves versus time are extracted from potentiodynamic polarization curves, offset to the anodic potential up to the pitting potential, for aged samples of 17-4PH stainless steel, A, B and C.

In summary, potentiodynamic polarization measurements reveal that in B, ageing at 550 °C, leads to the optimum corrosion resistance including higher OCP, pitting potential and passivity potential domain. On the other hand, sample C (ageing at 620 °C) results in the worst corrosion resistance. This is an indication of existence of a marked microstructure difference in C which can be attributed to volume fraction of ferrite, morphology and distribution of copper rich precipitates and the amount of reverted austenite [2)].

Concerning the influence of reverted austenite, it has been reported that copper precipitates, are expected to be a favorable nucleation site for reversed austenite, since both copper and austenite have the same FCC structure with the similar lattice parameter. During ageing at high temperature above 600 °C, segregation and diffusion of austenite stabilizer's Cu, Ni and Fe atoms would have a profound influence on the precipitates and the martensite matrix, leading to austenite forming elements enriched areas around the copper precipitates, which could trigger reversed austenite to nucleate. Cr content which is ferrite former conversely decreases the reverted austenite. Therefore, C and N which are also austenite stabilizers may concentrate an the reverted austenite. Moreover, the growth of reversed austenite attracted considerable amounts of Cu and Ni from the martensite matrix, since the solubility of these elements in austenite was much higher [2,5)]. The reverted austenite was a stable phase only in the C condition (sample aged at 620 °C) which encompassed the ε-copper rich precipitates. This phenomenon has not been reported in A and B [2)]. The overall effects of the above parameters are expected to be the reason higher galvanic current was monitored in C compared to A and B. In addition, the presence of white lamellar recrystallized alpha ferrite, which has the highest value in C (both in size and volume fraction) [5)], could also be another reason which helps to explain different currents observed in A, B and C. This phase does not exist in A. In A (sample aged at 480 °C), during precipitation of copper, coherent BCC clusters nucleate and by increasing the ageing temperature in B, they grow in the supersaturated BCC matrix, loose slightly their coherency and then by further increasing of ageing temperature in C, they subsequently transform to incoherent FCC ε-copper rich precipitates reaching a certain critical size around 30 nm [2,17)]. Therefore, coarsening and lowering coherency of precipitates in higher ageing temperature results in the lower corrosion resistance in C. More investigations with accurate techniques such as TEM are needed to determine the microstructure influence and corrosion initiation sites, and to illuminate the exact mechanism.

In order to observe morphology of pits, anodic polarization of samples was carried out close to their pitting potential. Formation of several metastable and stable pits in sample aged in A, B and C was observed and the micrographs were shown in Fig. 4.

Fig. 4 illustrate stable pits morphology with lacy cover over pits formed at sample aged at 620 °C. Formation of a few metastable pits in other conditions, A and B was also detected.

4. Conclusion

The aim of this work was to study the effect of ageing treatment on the corrosion behavior of 17-4PH stainless steel in 3.5% NaCl. The results can be summarized as follows;

The slow scan rate potentiodynamic polarization revealed that by increasing ageing temperature from 480 to 550 °C, the pitting potential is considerably increased, but further rising the ageing temperature up to 620 °C reduces the pitting potential. This is an indication of existence of a marked microstructure difference in sample aged at 620 °C which can be attributed to volume fraction of ferrite, morphology and distribution of copper rich precipitates and the amount of reverted austenite. Microscopical observation after anodic polarization close to pitting potential, also confirmed the formation of several metastable and stable pits in sample aged at 620 °C.

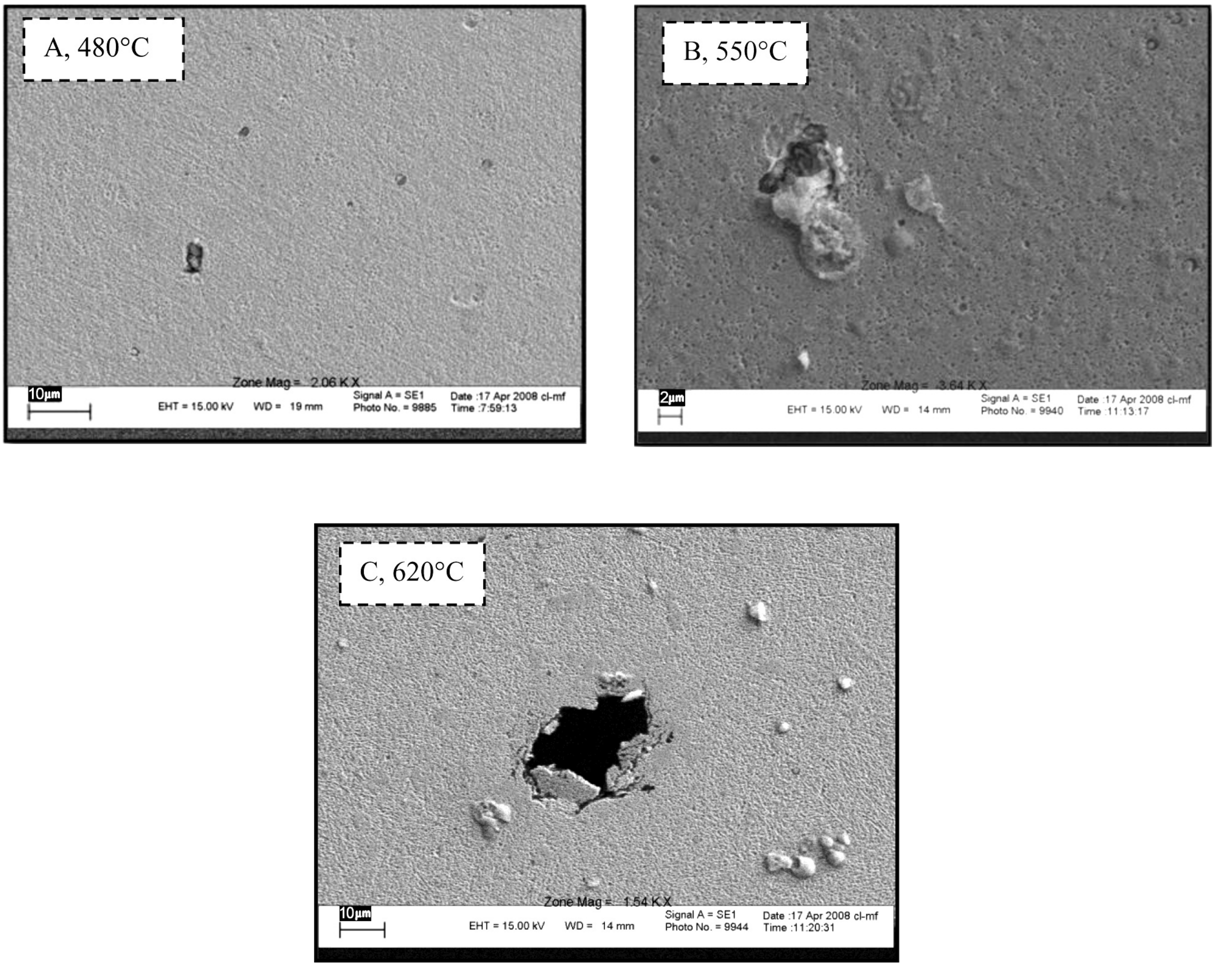

Fig. 4. Pits morphology of aged 17-4PH, after anodic polarization close to their pitting potential.

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