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Effect of molybdenum on SCC of 17-4PH stainless steel under different aging conditions in chloride solutions

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Type 17-4 PH martensitic precipitation-hardenable stainless steel, having a combination of high mechanical properties and good corrosion resistance is widely used in aerospace, chemical, and petrochemical and food industries This alloy has a high resistance to stress corrosion cracking but age hardening treatment, increases its sensitivity to stress corrosion cracking. There are several works investigating the influence of different aging treatments on the microstructure, mechanical properties and corrosion resistance of 17-4 PH steels, however there are little works studying the simultaneous effects of aging treatments and molybdenum content on corrosion properties of these steels. In this research, the effect of molybdenum on stress corrosion cracking resistance of 17-4 PH alloy using U-bend samples in chloride solutions, as well as its effect on passivity, has been investigated. Quantometer, Scanning Electron Microscope(SEM) and potentiostat were used to determine the chemical composition, microstructure and anodic polarization behavior of the alloys. It is found that molybdenum has a useful effect on stress corrosion cracking resistance under the peak aged conditions, and this is because of development of delta-ferrite phase by increasing the molybdenum content and subsequently decreasing the strength of the alloy. © *2006 Springer Science + Business Media, Inc.*

1. Introduction

Precipitation-hardening stainless steel type 17-4 PH has been widely used as structural components in various applications, such as nuclear, chemical, aircraft and naval industries due to their excellent mechanical properties, good fabrication characteristics and good corrosion resistance [1].

From basic electrochemistry principles, stainless steels having very negative primary passivation potentials (E_{pp}) and small critical current densities for passivation (i_c) normally passivate quite readily in aqueous environments. Once passivated, the alloys will normally corrode at very low rates in accordance with Faraday's Law and their passive current densities (i_p). If the oxidizing characteristics of the environment are overly powerful, alloys can be spontaneously polarized to potentials sufficiently noble (positive) that they will be subjected to accelerated corrosion and pitting attack in the transpassive potential region (that is, corrode at the high current densities associated with the potentials more noble than E_{tp}). The effect of molybdenum in increasing the pitting resistance of stainless steels in acid solutions is well documented [2, 3]. Truman *et al.* have shown that increasing the molybdenum content of the ferritic stainless steels will expand the passive region of these alloys by increasing E_{tp} and simultaneously by decreasing E_{pp}. They also have shown that by adding molybdenum to austenitic stainless steels, their resistance to stress corrosion cracking (SCC) will increase [3].

There are several works investigating the influence of different aging treatments on the microstructure, mechanical properties and corrosion resistance of 17-4 PH steels [4–8]. However, there are little works studying the simultaneous effects of aging treatments and molybdenum content on corrosion properties of these steels. Raja et al. have used the hardness as a criterion for stress corrosion cracking resistance of 17-4 PH stainless steels at different aging temperatures. Their results showed that a maximum hardness of 33 RC is required for good resistance to SCC and also the peak-aged samples have the most

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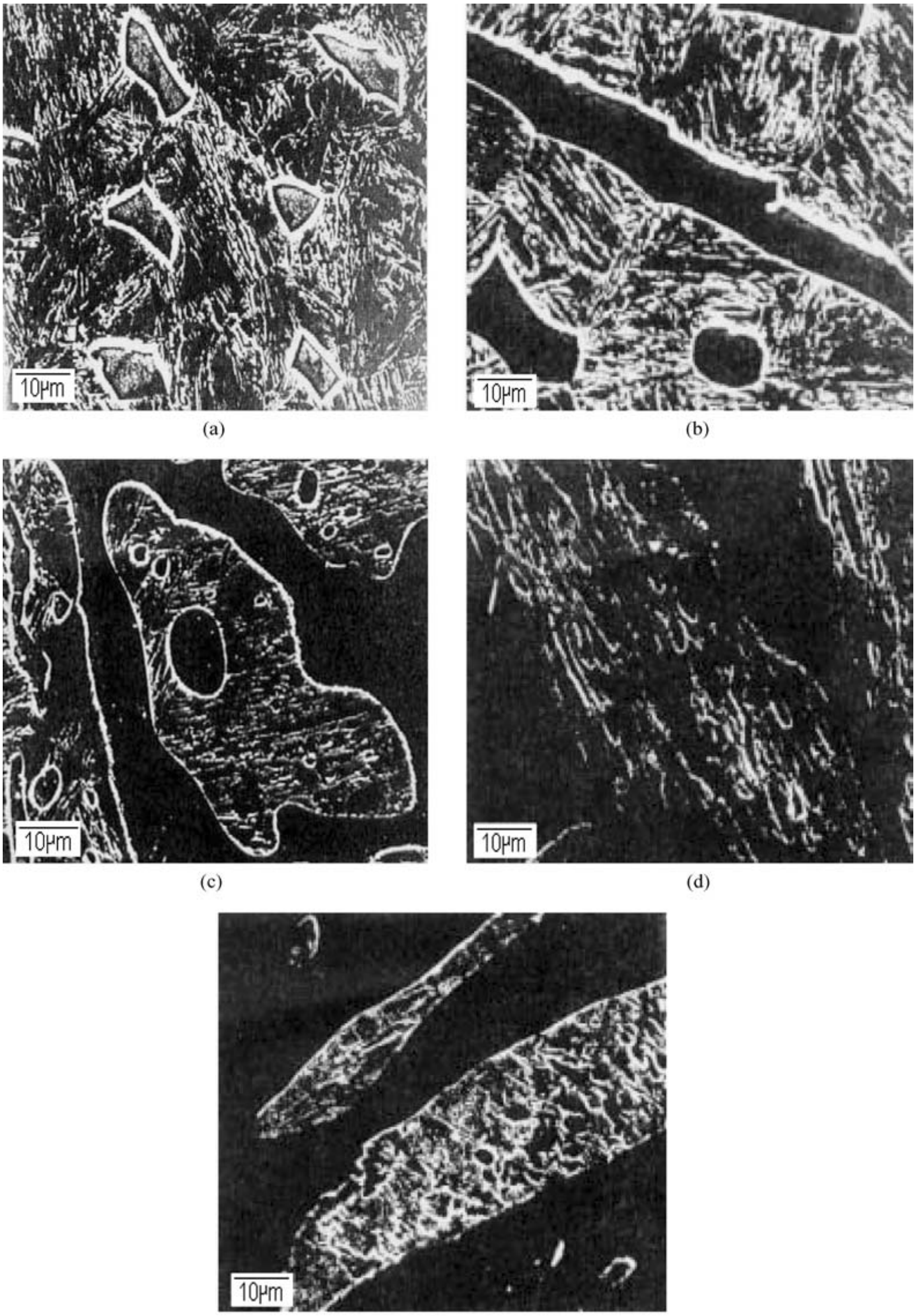

(a) (b) (c) (d) (e)

Figure 1 SEM micrographs of the alloys with different Mo content at peak aged conditions. a: 0%, b: 0.5, c: 0.7, d: 1.59 and e: 2.4 wt.% Mo.

susceptibility to this kind of corrosion [9]. In this work the Simultaneous effects of Mo content on the stress corrosion cracking resistance and passivation behavior of these steels under different ageing conditions are investigated.

2. Experimental procedures

Five 17-4 PH stainless steel alloys with different amounts of molybdenum were investigated in this work. The alloys were melted in an induction furnace and cast in ceramic molds. Quantometric analysis was done for determining the chemical composition of these alloys as shown in Table I. The samples were prepared in dimensions 90 × 10 × 1 mm by machining the cast blocks and then solution treated at 1050°C for 1 h. Three different aging heat treatments were conducted on the samples as following:

TABLE I Chemical compositions of the alloys (wt%)

Sample no.	%P&S	%Nb	%Cu	%Mo	%Ni	%Cr	%Mn	%Si	%C
1	0.002	0.384	3.56	0	3.66	15.5	0.64	0.95	0.054
2	0.02	0.374	3.41	0.5	3.64	15.4	0.57	0.88	0.051
3	0.02	0.459	3.51	0.7	3.63	15.8	0.65	0.86	0.051
4	0.02	0.482	3.43	1.59	3.45	16.1	0.52	0.89	0.05
5	0.02	0.485	3.41	2.42	3.4	16	0.5	0.85	0.049

1. Peak aged: heat treated at 482°C for one hour and then air cooled.
2. Semi-overaged: heat treated at 550°C for two hours and then air cooled.
3. Overaged: heat treated at 600°C for four hours and then air cooled.

The microstructures of samples with different Mo content at peak aged conditions were studied by SEM model Camscan MV2300.

U-bend samples in chloride solutions were used to investigate the stress corrosion cracking resistance of the alloys. These samples were prepared according to G-30–79 ASTM standard and the electrolyte used was the 3.5% NaCl solution with pH equal to two adjusted by HCl. In order to measure time to failure, samples were partially immersed in the electrolyte under OCP potential.

Anodic polarization tests for the alloys were conducted potentiodynamically using potentiostat/Galvanostat 263A (EG&G) Princeton Applied Research, at a scan rate of 1 mV/s to determine the passivity parameters such as critical pitting or transpassive potential (E_{tp}), the primary passivation potential (E_{pp}), the critical anodic current density (I_c), and passive current density (i_p). The electrochemical cell for the anodic polarization test consisted of a 1 L multinecked flask, as specified in ASTM G5, with a platinum counter electrode and a saturated calomel electrode (SCE) positioned in a salt bridge with a high-silica tip [10].

3. Results and discussion

Fig. 1 shows the microstructures of 17-4 PH stainless steels with different Mo content at peak aged conditions. These microstructures consist of martensite and ferrite. The volume fraction of ferrite in this figure increases as the amount of Mo in the steel increases. This is due to the fact that Mo is a ferrite stabilizer by decreasing the amount of eutectoid carbon and increasing the eutectoid temperature and therefore shrinkaging the area that austenite is stabilized [3]. The percentage of ferrite determined by point counting method for the samples is shown in Fig. 2. These results have good agreement with Schoefer diagram [11]. The variations of hardness with Mo content of the samples in different aged conditions are shown in Fig. 3. As expected, in all of the aging conditions the hardness of the sample whose Mo content is negligible, is maximum. Also the maximum hardness belongs to the sample with negligible Mo content in the peak aged condition.

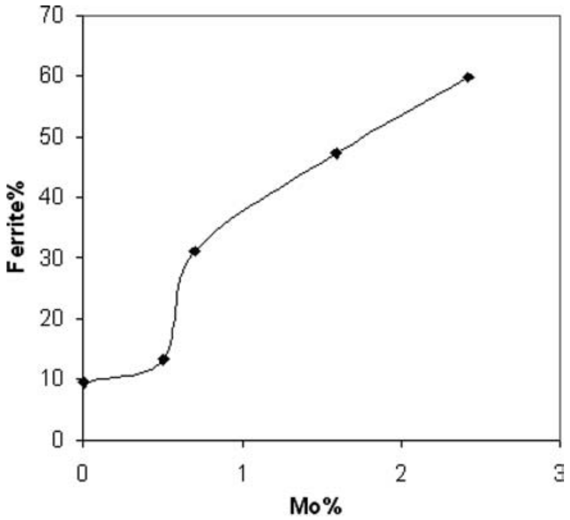

Figure 2 Percent of ferrite as a function of Mo content in the peak aged samples.

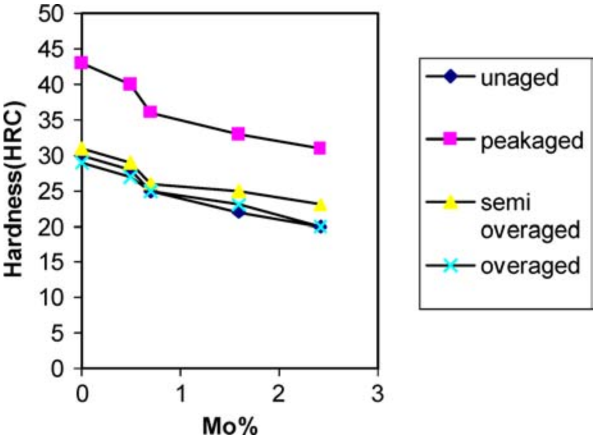

Figure 3 The variations of hardness with Mo content of the samples for different aged conditions.

The time to fracture of samples with different amounts of Mo under peak aged condition in 3.5% NaCl solution (pH = 2) are shown in Table II. The SCC resistance of the sample with maximum Mo concentration is the highest. This Table shows that the SCC resistance of the steel increase as the Mo content in the sample increases. Table III shows the same thing for the samples under semi-aged condition. The only broken sample is the one with negligible amount of Mo. Comparing Tables II and III shows that the samples under semi-overaged condition have better resistance to SCC than samples under peak

TABLE II Time to failure of samples with different amount of Mo under peak aged conditions in 3.5% NaCl solution (PH = 2)

Sample no.	%Mo	Time to failure (h)
1	0	38
2	0.50	60
3	0.70	120
4	1.59	240
5	2.42	Not failed

TABLE III Time to failure of samples with different amount of Mo under semi-overaged conditions in 3.5% NaCl solution (pH = 2)

Sample no.	%Mo	Time to failure (h)
1	0	300
2	0.50	Not failed
3	0.70	Not failed
4	1.59	Not failed
5	2.42	Not failed

aged condition. This result shows that in determining the SCC susceptibility of the samples the hardness is not the main criteria and other factors have important effect on this matter.

The anodic polarization behavior of the samples with different amount of Mo under peak aged condition measured potentiodynamically in 3.5% NaCl solution (pH = 2) at room temperature is shown in Fig. 4. All of the alloys except sample with 0% Mo showed typical anodic polarization curves comprising an active, a passive and a transpassive region. Significant insight regarding corrosion behavior can be obtained from the analysis of data obtained from these anodic polarization tests.

From the introductory discussion, the desirable anodic polarization characteristics for 17-4 PH stainless steels would be (a) low values of i_c, (b) very negative values for E_{pp}, (c) low values of i_P, (d) highly positive values for E_{tp}, (e) large potential differences between E_{pp} and E_{tp}

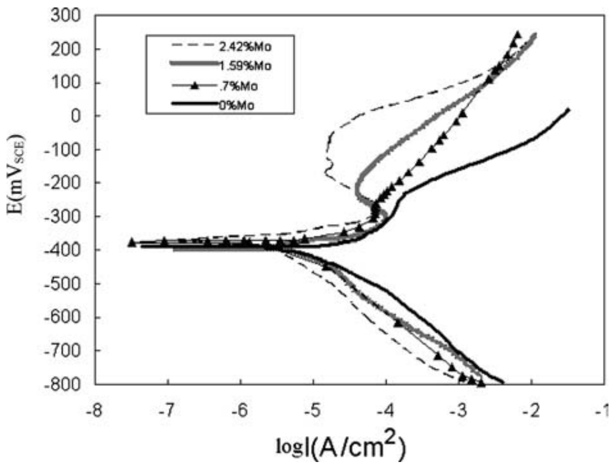

Figure 4 The anodic polarization behavior of the samples with different amount of Mo under peak aged condition, measured potentiodynamically in 3.5% NaCl solution (pH = 2) at room temperature.

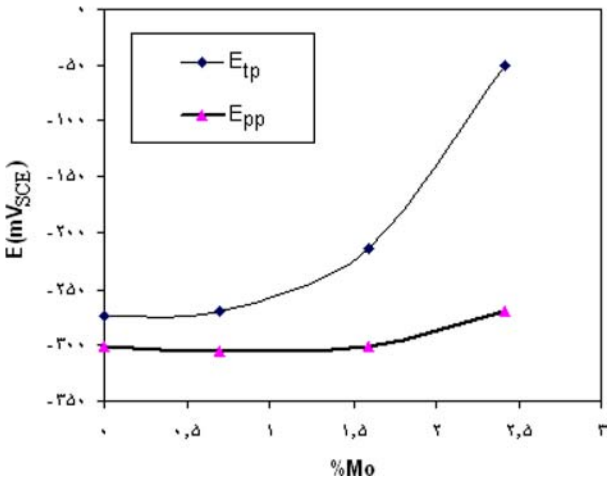

Figure 5 Effect of Mo content on the E_{tp} and E_{pp} of the alloys under peak aged conditions in 3.5% NaCl solution (pH = 2) with scan rate of 1 mV/S.

Addition of molybdenum to the alloys displaced E_{tp} in the active direction and decreased I_c and the passive current (I_p). A measure of the pitting corrosion resistance of the alloy is given by the difference between the transpassive potential, E_{tp} (breakdown potential) and the primary passivation potential, E_{pp}. As it can be seen from Fig. 4, E_{tp} for the samples increases considerably as the amount of Mo increases. E_{pp} does not change much and except for 2.42% Mo sample, it is almost constant so, as Fig. 5 shows ($E_{tp}-E_{pp}$) increases and as a result the passive range increases considerably by increasing the Mo content. In the case of ferritic stainless steels the passive region expanded by increasing E_{tp} and simultaneously by decreasing E_{pp} [3] as mentioned earlier. It means Mo did not facilitate oxide film formation in 17-4 PH alloys as it did for ferritic stainless steels but, once the film was formed it becomes more resistance to oxidizing environment and pit will initiate at higher potentials with increasing Mo content.

4. Conclusions

1. The susceptibility of stainless steel 17-4 PH to SCC is maximum under peak-aged condition and is minimum under solution treatment (unaged) condition.
2. With increasing the Mo content of the steel, the amount of delta-ferrite increases and consequently hardness of the sample decreases.
3. Although the hardness of peak-aged samples is higher than semi-overaged samples, the latter showed more resistance to SCC.
4. Using hardness as a criterion for resistance to SCC can be misleading.
5. I_c and I_{pass} for the samples decreases as the amount of Mo in the samples increases.

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