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PITTING OF Fe-Mn-Al ALLOYS IN NaCl SOLUTION

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Key words: Fe-Mn-Al alloys, corrosion, NaCl solution, pitting, ferrite, austenite, two-phase alloys.

ABSTRACT

Five Fe-Mn-Al (Femnal) alloys with the ferrite contents varied from 0.5% to 98% were tested in 3.5% NaCl at room temperature. Both potentiodynamic polarization and immersion test were performed. In deaerated solution, the corrosion potentials were very close for these alloys. The passive current increased and the width of the passive region decreased with the increase of ferrite content. However, the nearly ferritic alloy showed much better passivation behavior, presumably due to the addition of 6% Cr. In aerated solution, no or very small passive region was observed. From the immersion test, the general corrosion was found to be minor. Pitting corrosion was the primary corrosion except for the ferritic alloy. The pits were found more frequently in the ferrite phase or at the interface between the ferrite and austenite phases.

INTRODUCTION

Stainless steels based on the alloying elements of Cr and Ni are used worldwide in corrosive environments. Because of strategic character of both chromium and nickel, there raised some hope several years ago, when the new *Fe-Mn-Al* ternary alloys were introduced as the next possible candidate for corrosion applications.

As concluded from the comparison between *Fe-Cr-Ni* and *Fe-Mn-Al* alloys [1], the mechanical properties are comparable in a wide range of temperature - from cryogenic up to elevated. It has been confirmed that the Femnal alloys have superior creep resistance [2,3]. They also have good oxidation resistance up to 850°C [4-6]. Hydrogen embrittlement (HE) of the Femnal alloys has been reported [7-9]. The interface between austenite and ferrite was observed to be critical for the HE [8]. The measurement with a wide range of austenite/ferrite ratios showed that the degree of HE increased as the ferrite content increased. The alloy with a full austenite phase was essentially

immune to HE [9]. As for the stress corrosion cracking (SCC) properties, it was observed that the ferritic phase and the interface along the ferrite and austenite were susceptible to the cracking in the solution containing Cl ions [10-11]. An anodic overpotential would lead to the decrease of the SCC susceptibility of the *Fe-8.7% Al-29.7% Mn* alloy [12]. The ability of passivation was found very poor for the same alloy if tested in 1N sulfuric acid solution [13]. On the other hand, the general corrosion was found minor for the duplex Femnal alloys. Pitting was the main degradation factor [14]. Pits were observed mainly in the ferritic phase. A strong dependence of the electrochemical polarization on the concentration of NaCl has been reported [15]. The passive current density for Femnal alloys was higher than that for AISI 316 stainless steel by one order of magnitude [14,16].

In the present work, the corrosion resistance of the femnal alloys was further studied. Alloys with the ratios of ferrite/austenite from 0.5% to 98% were tested in 3.5% NaCl solution. The different corrosion characteristics of the ferrite and austenite phases were

examined.

EXPERIMENTAL

The tests were carried out with five Femnal steels covering a wide interval of austenite/ferrite ratios. The chemical compositions of the alloys are given in Table 1. The processing and typical microstructures of these alloys have been described previously [9]. Two experiments were performed in 3.5% NaCl solution at room temperature: electrochemical potentiodynamic polarization and immersion tests.

The potentiodynamic polarization curves were measured in both aerated and deaerated solutions. The test cell involved a gas bubbler, a saturated calomel reference electrode (SCE), and a graphite counter electrode. The specimens were ground by SiC paper to 1200 grit. The exposed area varied from 0.7 to 0.9 cm².

The scanning rate was normally selected at 1mV/s. Some additional measurements were conducted with the scanning rates of 0.2 and 10mV/s. For each condition, at least two specimens were used. In the case of deaerated condition, the solution was prebubbled for 24 hours and the bubbling continued during the test.

The immersion test was carried out in several 2-liter beakers. Specimens with the dimensions of 9mm × 9mm × 1.3mm were tested. The surfaces of the specimens were ground to 1200 grit with SiC paper, cleaned, and dried. The lengths of immersion time were 2, 4, 7, 14, and 21 days. The specimens once taken out from the solution were not used for the next immersion. The surfaces of the specimens were sys-

tematically examined under an optical microscope.

RESULTS AND DISCUSSION

Fig.1 presents the potentiodynamic polarization curves for the alloys in deaerated 3.5% NaCl solution at room temperature. The electrochemical parameters are summarized in Table 2. As can be seen, the corrosion potentials of the alloys varied in a very narrow range, from -871mV to -789mV. The most noble potential was obtained for alloy A. Passivation was observed for all alloys. Except for alloy E, the width of the passive region was found to be a decreasing function of the ferrite content (falling from 360mV for alloy A to 119mV for alloy D). The passive region became flatter and larger for alloy E. There were only small differences in the minimum passive currents for alloys A to D. They were in the range of 17-35 $\mu\text{A}/\text{cm}^2$. On the other hand, the passive region of alloy E lied below those of other alloys, with a minimum value of 4 $\mu\text{A}/\text{cm}^2$. Because of the increasing passive current of alloys A to E, it appeared that a higher content of ferrite led to a higher sensitivity to the corrosion attack. In the case of alloy E, which was nearly fully ferritic, the addition of 6% of chromium was likely the reason for the decrease of the passive current and the broader passive region.

As for the pitting potential, the noblest potential was recorded for alloy A. When the ferrite content increased from alloy B to D, the pitting potential became more negative. Alloy E must be considered separately again, because of different shape of the polarization curve. Although the increase of the cur-

Table 1. Chemical Compositions (Weight Percent) and Ferrite Contents of the Alloys

Alloy	Mn	Al	C	Cr	α (Pct)
A	28.52	9.97	1.047	—	0.5
B (avg)	29.60	10.19	0.832	—	10
(α)	24.39	11.26	—	—	—
(γ)	30.04	9.62	—	—	—
C (avg)	28.63	10.45	0.498	—	35
(α)	26.66	9.79	—	—	—
(γ)	31.36	8.22	—	—	—
D (avg)	29.99	10.19	0.305	—	65
(α)	28.13	10.33	—	—	—
(γ)	32.25	8.81	—	—	—
E	21.50	9.86	0.330	6.23	98

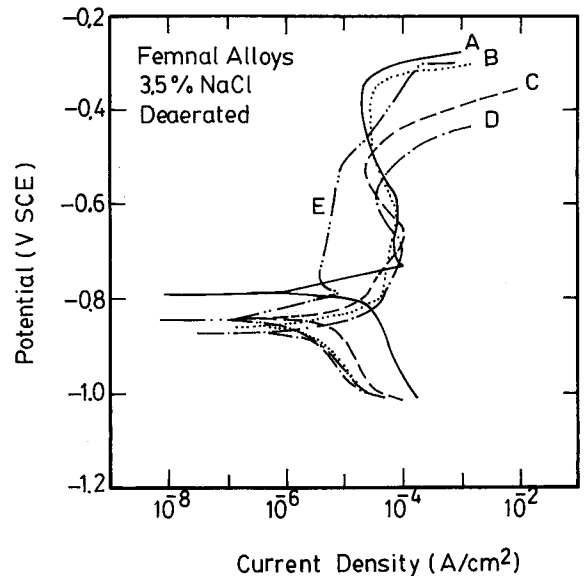


Fig. 1. Potentiodynamic polarization curves of the alloys in deaerated 3.5% NaCl solution. Scanning rate: 1mV/s.

Table 2. Electrochemical Parameters of the Alloys in 3.5% NaCl

Alloy	Solution treatment	E_{corr} (mV SCE)	E_{cr} (mV SCE)	E_{pp} (mV SCE)	i_{p} ($\mu\text{A}/\text{cm}^2$)
A	deaerated	-789	-728	-335	17
B	deaerated	-859	-637	-365	26
C	deaerated	-839	-668	-505	23
D	deaerated	-871	-698	-555	35
E	deaerated	-840	-790	-520	4
A	aerated	-325	—	—	—
B	aerated	-382	—	—	—
C	aerated	-400	—	—	—
D	aerated	-452	—	—	—
E	aerated	-354	—	—	—

E_{corr} : corrosion potential

E_{cr} : critical potential for active-passive transition

E_{pp} : pitting potential

i_{p} : passive current density, minimum value

rent started at a quite negative value of -520 mV, the curve was much less steep than the other alloys.

The influence of the scanning rate on the polarization curve was studied for alloy *D*. As can be seen from Fig.2, there was no difference in the corrosion potentials. In the passive region, a lower scanning rate led to a lower passive current. This result showed that the corrosion process, especially the passivation, was a time dependent process for this alloy. At a scanning rate of 10 mV/s, there was no sufficient time for passivation. At 0.2 mV/s, the width of the passive region became larger, compared with that for 1 mV/s.

If tested in the aerated solution, the corrosion potentials of all alloys were shifted to more positive values approximately by 0.5V, as shown in Fig.3. The corrosion potentials are also listed in Table 2 for comparison. They were again in a narrow interval, between -325mV (alloy A) and -452mV (alloy D). The higher ferrite content led to a lower value. Alloy *E* was an exception. Its corrosion potential was increased to -354mV. The passivation region was not present for all alloys except that alloy *E* seemed to have a small extended region. The potentials for rapid rise of current in the anodic region varied with the ferrite content, similar to the pitting potentials in the deaerated solution. On the other hand, alloy *E* showed the highest resistivity to the pitting damage.

During the immersion test, specimens of alloys A, B, C, and D were covered by a layer of stain soon after the immersion had begun. For these alloys, the color of the stain appeared to be darker and the stain became thicker for longer immersion time. For alloy

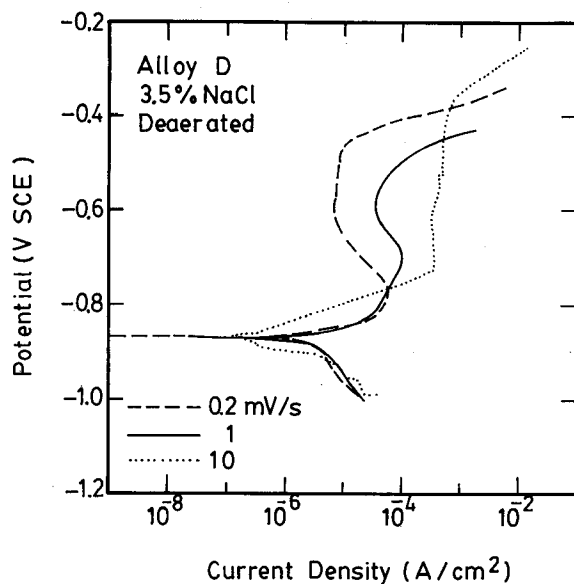


Fig. 2. Potentiodynamic polarization curves for alloy *D* at different scanning rates in deaerated solution.

E, on the other hand, even after 3 weeks of immersion test, no stain was observed at all on the surface except that some crevice corrosion took place near the fixing points. Some larger pits were also observed on the edges.

For the metallographic study, the stain was polished off and the surface was examined under an optical microscope. It was found that the darker stain was always originated from some pits. For the areas

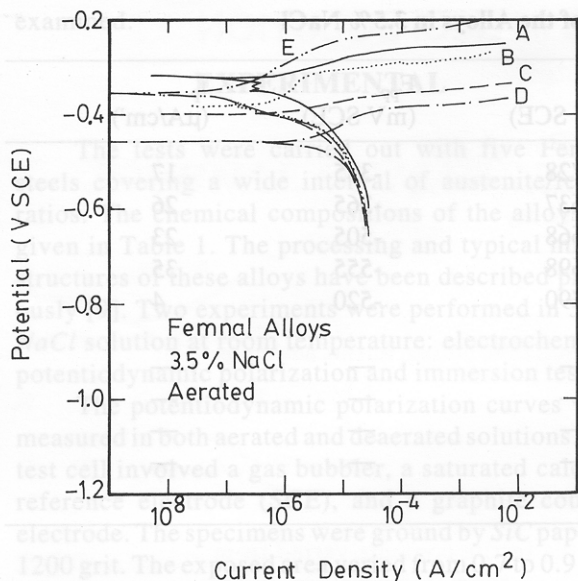


Fig. 3. Potentiodynamic polarization curves of the alloys in aerated 3.5% NaCl solution. Scanning rate: 1mV/s.

free of pitting, only a thin layer of stain was present. This implied that the general corrosion was not significant and pitting was the primary type of corrosion for alloys A to D. The favorable sites for pit nucleation were the ferrite grains and the ferrite/austenite interfaces. Once nucleated, the pits would only grow within the ferrite grain or along the interface. For example, Fig.4 shows the optical micrograph of alloy C after seven days of immersion test. Most of the pits were positioned within the ferrite grains. Some were present at the interface. Since the ferrite grains were the preferential sites for pitting, the maximum size of the pits was limited by the grain size of the ferrite phase. For alloy E, except near the edge of the specimens, no pit was observed. This demonstrated the benefit of addition of Cr for the corrosion resistance.

CONCLUSIONS

1. For Femnal alloys, polarization tests indicated that higher content of ferrite led to a smaller passive region and a higher passive current. With 6.23% Cr in alloy E, the passivation properties were greatly improved.
2. The passivation was dependent on the scanning rate. A lower scanning rate allowed more time for passivation.
3. During the immersion test, pitting was the primary type of corrosion. Pitting occurred preferentially in the ferrite grains or along the interface between ferrite and austenite. The severity of pitting increased with the ferrite content. However, alloy E showed good resistance to pitting due to the addition of Cr.

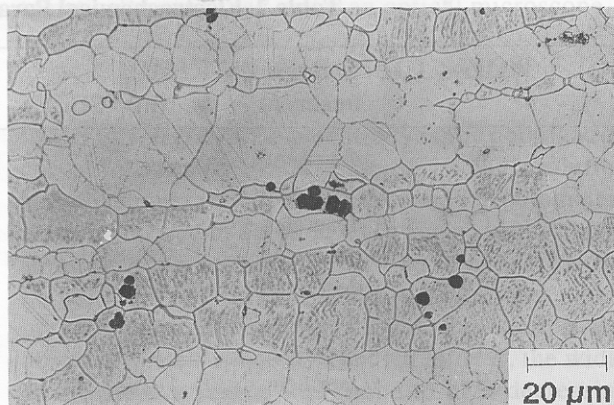


Fig. 4. Pitting morphology of alloy C after immersion test for seven days.

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