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計畫主持人：劉增豐

計畫參與人員：李堅瑋、郭柏村、王承舜、段玉軒、蘇俊瑋、林志龍

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Effects of Carbon Content on Pitting Corrosion and As-quenched Microstructure in Fe-8.8Al-30Mn-4Cr-C Alloy

* 李堅璋*、郭柏村、王承舜、段玉軒、蘇俊瑋、林志龍、劉增豐

交通大學材料科學與工程學系
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The pitting corrosion behaviors of the as-quenched Femac alloys with various carbon contents in the range from 0.06 to 1.58 wt.% were studied by potentiodynamic polarization and immersion tests. In martensitic Femac alloys, the 18R martensites results in much favorable sites for the pitting nucleation between the martensites and the α matrix. Owing to the present of the 18R martensite, Even if the increased volume fraction of the γ phase with increasing the carbon content, there is no obvious rise in the critical pitting potential. Besides, the pitting resistance of the duplex Femac alloy can be noticeably improved as a result of the absence of the 18R martensite. In the meanwhile, the α/γ grain boundaries substitute the initial pitting sites for the 18R martensites in the duplex Femac alloys. When the carbon content was high enough to form the fine κ' -carbides within the austenite matrix, the lower coherent interfacial and strain energies would have no detrimental effect of the existence of the fine κ' -carbides on the pitting corrosion resistance. The retained inclusions of manganese sulfide and aluminum oxide, however, are responsible for the deterioration in the pitting resistance of the austenite phase.

Keywords : Carbon 、Fe-Al-Mn-C alloy 、Pitting Corrosion 、microsturcture

Introduction

Although the Fe-Mn-Al-C alloys possess the excellent mechanical and physical properties, the relatively lower corrosion resistance restricts their extensive applications in industry. For the Fe-Mn-Al-C based alloys, the pitting attack is the primary corrosion behavior rather than the general corrosion [1-3]. It is known that the pitting corrosion is strongly related to the microstructural factor. The variation in carbon content has an important influence on the microstructural changes in the Fe-Mn-Al-based alloys. So far, most investigations on the corrosion of the Fe-Mn-Al-based alloys were focused on the electrochemical corrosion measurements [3-6]. However, the information concerning the effect of the microstructural changes on the pitting corrosion behaviors is presently deficient. Therefore, the aim of this study is to determine the relationship between the as-quenched microstructure and the susceptibility to the localized pitting corrosion in the Fe-Mn-Al-Cr-C alloys as a function of carbon content by means of transmission and scanning electron microscopy.

Experimental Procedure

The alloys examined in the present study were prepared in a air induction furnace by using 99.9 % iron, 99.7 pct aluminum, 99.9 pct electrolytic manganese, 99.6 pct chromium, 99.5 pct nickel and pure carbon powder. After being homogenized at 1150 °C for 72 hours, the ingots were sectioned into 2-mm-thickness sheets. These sheets were subsequently solution heat-treated at 1150 °C for 3 hours followed by a rapid quench into iced water. The chemical compositions of the present alloys were analyzed by inductively coupled plasma-mass spectrometer (ICP), as show in Table I. The pitting corrosion behaviors were studied by potentiodynamic polarization and immersion tests. All samples were analysis by OM, TEM and SEM for microstructure observation and chemical composition.

Results and Discussion

A. The effect of the carbon content on the potentiodynamic polarization curve

Figure 1 shows the polarization curves of these seven Femac alloys. The results of critical pitting potential and current density determined from each polarization curve are listed in Table II for comparison. It is apparent that there is a general tendency towards a higher critical pitting potential with a higher carbon contained Femac alloy. From the experimental results, the variations in the critical pitting potentials of the Femac alloys are worthy to note. For the Femac alloy with carbon content in the range from 0.06 to 0.61 wt.%, there is a slight increase in the critical pitting potential with increasing the carbon content. However, both the relatively obvious rises can be observed as increasing the carbon contents from 0.61 to 0.72 and 0.72 to 0.93 wt.%. Subsequently, when the Femac alloys contain higher carbon contents from 0.93 to 1.58 wt.%, the critical pitting potentials are almost kept. Therefore, it can be inferred from the potentiodynamic polarization test that the pitting resistance of the Femac alloy can be effectively improved until up to 0.93 wt.% carbon content, but it does not increase any more with further increasing from 0.93 to 1.58 wt.%.

B. TEM and SEM investigations on the as-quenched microstructures

Figure 2(a) is a SEM of the as-quenched Femac-0.06C alloy, exhibiting ferrite grains and precipitates within the grains. Figure 2(b), a higher magnification micrograph taken from the α grain interior, clearly reveals the formation of needle-like precipitates with specific orientations. In order to identify the needle-like precipitate, TEM examination of thin foils was performed. Figures 2(c) through (e) are a BF electron micrograph and two SADPs taken from the needle-like precipitate and its surrounding α matrix, indicate that the needle-like precipitates are 18R martensites. The structure of the 18R martensite was further determined by the HRTEM with the aid of computer simulation to be between 18R(42)₃ and 18R(51)₃, and the average

stacking sequence of $\{111\}_{\text{FCC}}$ plane in this martensite is $(4.1915, 1.8085)_3$ ^[7,9,10]. Despite the controversy over the structure, it is interesting in this study whether the needle-like 18R martensites will significantly affect the susceptibility to the pitting corrosion or not.

Figure 3(a) is a SEM graph of the as-quenched Femac-0.32C alloy. A high density of the needle-like 18R martensites can still be found within the α grains, as shown in Figure 3(b). It is worthy to note that wide and rather narrow martensite-free zones (MFZs) inside the ferrite grains can be seen along the α/γ grain boundaries and the α/α grain boundaries, respectively. The MFZs are thought to be due to the depletion of the carbon atoms which diffused to the nearby γ phases having a higher carbon solubility in comparison with the α phase ^[8]. Otherwise, the width of the MFZs should be similar regardless of kinds of grain boundaries.

Along with increasing the carbon content to 0.61 wt.%, in addition to the increase in the volume fraction of the γ phases, there is no difference in the microstructural constitution between the Femac-0.32C and Femac-0.61C alloys, as shown in Figures 4 (a) and (b). The needle-like 18R martensites and the MFZs could still be found in the Femac-0.61C alloy. In contrast to the Femac alloys with 0.06, 0.32 and 0.61 wt.% carbon, the formation of the 18R martensites within the discrete ferrite grains in the Femac-0.72C alloy is absent, as shown in Figure 5. The microstructure of the alloy is composed of the duplex phases of γ and α . Figure 6 is a scanning electron micrograph of the Femac-0.93C alloy in the as-quenched condition, exhibiting a single-phase γ with annealing twins. Also, no precipitates could be detected within the austenite phase by either SEM or TEM.

Figure 7(a) shows a scanning SEM graph of the as-quenched Femac-1.25C alloy. The morphology may suggest that the microstructure is still a single-phase γ . However, the BF electron micrograph reveals that a high density of fine precipitates with a modulation structure was formed within the γ matrix, as can be seen in Figure 7(b). Figure 7(c), a SADP indicates that the fine precipitates are $(\text{Fe,Mn})_3\text{AlC}_x$ carbides (designated as κ' -carbides) having an $\text{L}'1_2$ -type structure ^[11]. The existence of the satellites demonstrates that the fine κ' -carbides were formed during quenching by a spinodal decomposition. Figure 7(d) is a (010) κ' -carbides DF electron micrograph of the as-quenched Femac-1.25C alloy.

C. SEM observations on the pitting corrosion behaviors

In order to investigate the susceptible areas and the modes of pitting attack, the present specimens were test by immersion test in 6 wt.% ferric chloride solution. Moreover, the fresh specimens were held at potentials just slightly above their critical pitting potentials in a 3.5 wt.% sodium chloride (NaCl) solution at room temperature to accelerate the pitting corrosion and then examined by the SEM to observe the behavior of the pit propagation. The localized attacks are clearly found to be around the 18R martensites in the initial stage of the pitting corrosion after the Femac-0.06C alloy was immersed in $\text{FeCl}_{3(\text{aq})}$ for a short time period, as shown in Figure 8(a). With raising immersing time, there are a large number of growing pits in the interiors of the α

grains but along the α/α grain boundaries, as shown in Figure 8(b). This indicates that the 18R martensite is much more susceptible to the pitting attack than the α/α grain boundary. Figure 8(c) exhibits a severely corroded surface after applying a pitting potential to the Femac-0.06C alloy, revealing that the pitting attacked areas extend to the α/α grain boundaries and the whole ferrite grains.

For the Femac-0.32C alloy, the 18R martensite interfaces also acts as the nucleation sites for the pitting corrosion in the immersion test and the subsequent attack causes pits to coarsen and grow inside the α grains, as shown in Figures 9(a) and (b). Based on the EDS analysis, it is verified that such pits occurred inside the γ grains are attributed to two kinds of inclusions. One is the manganese sulfide and the other is the aluminum oxide, which were produced during the melting process and retained in the ingot as solidifying. Figure 9(c) shows that the whole α grains were severely corroded after applying a pitting potential to the Femac-0.32C alloy. From these observations, it is suggested that the pits initiated at the 18R martensite interfaces in the interiors of the α grains and then gradually grew towards the grain boundaries. However, on the other hand, in addition to a few pits due to the existence of the manganese sulfide and aluminum oxide inclusions, no other pits related to the microstructural factors could be found inside the γ grains. Compared to the Femac-0.32C alloy, the severely pitting attacked area is reduced with the increase in the volume fraction of the γ phase in the Femac-0.61C alloy, as shown in Figure 10. As can be seen in Figures 11(a) and (b), the nucleation of the pits occurred first at the α/γ grain boundaries rather than inside the α grains. Subsequently, the pitting attacks proceeded to the interior of the relatively small and discrete α grains. Although the mode of the pitting attack inside the α grains is quite different as increasing carbon content from 0.61 to 0.72 wt%, the existence of the inclusions is still the main reason to facilitate the pitting corrosion in the austenite grains.

In Figure 12(a), the pitting corrosion originating from the inclusions becomes predominant in the single-phase austenite, where the pits were dispersed at random within the γ matrix. It is seen in Figure 12(b) that the larger and deeper pits followed the inclusion-induced pits after applying a pitting potential to the Femac-0.93C alloy.

Figures 13(a) and (b) are two SEM graphs for increasing the carbon content to 1.25 or 1.58 wt.% after the immersion and accelerated pitting corrosion tests, respectively. Compared to the Femac-0.93C alloy, there appears to be no difference in the behavior of the pitting attack between the γ matrix with and without the precipitation of the fine κ' -carbides. The existence of the retained inclusions is believed to be the reason to cause the pitting corrosion in the austenite grains. There are no evidences that the pitting attack is related to the precipitation of the fine κ' -carbides.

D. Relationship between the pitting corrosion behaviors and the microstructures

On the basis of the above observations, some discussion in detail will be given below. The present Femac alloys can be classified into the three main groups,

namely the Martensitic, Duplex and Austenitic Femac alloys. The martensitic Femac alloys contain carbon contents in the range of 0.06 to 0.61 wt.%. They are called martensitic since the 18R martensites are formed within the α phase during quenching. In these alloys, great strain-fields accompanying by the formation of the 18R martensites are developed around the martensites, so that the interfaces between the martensites and the α matrix provide much favorable sites for the pitting nucleation. The 18R martensite interfaces were observed to be attacked by the pitting corrosion in preference to not only the α/α but also the α/γ grain boundaries. It is thus to suggest that the 18R martensite is the most sensitive to the pitting corrosion due to the great strain-fields around them. The absence of the pits in the vicinity of the α/γ grain boundaries in the alloys can be formed as a result of the wide MFZs along the α/γ grain boundaries. This leads to the pitting attack from the interiors of the ferrite grains to their grain boundaries in sequence. The alloys can be further subdivided into both with and without γ phase. The volume fraction of the γ phase is increased with increasing the carbon content ranging from 0.06 to 0.61 wt.%. Since the α grains contain a high density of the 18R martensites, the pitting corrosion resistance should be increased along with increasing the volume fraction of the γ and vice versa. However, no obvious rise in the critical pitting potential is expected while the 18R martensite is still present. Therefore, it is appropriate to propose that the martensitic Femac-0.06C alloy without the γ phase has the worst resistance to the pitting corrosion. Increasing carbon contents from 0.06 to 0.61 wt.% can somewhat improve the pitting corrosion resistance of the martensitic Femac alloys. This is in agreement with the results obtained from the potentiodynamic polarization test in Figure 1.

The present Femac alloy containing 0.72 wt.% belongs to one of the duplex Femac alloys. They are called Duplex since their microstructures essentially consist of duplex phase of austenite and ferrite in the as-quenched condition. The absence of the 18R martensite distinguishes the duplex from martensitic Femac alloys. Because the volume fraction of the α phase is further reduced with increasing the carbon content in the Femac alloy, the ferrite grains gradually change to smaller and discrete ones. Based on the reason for the formation of the MFZs mentioned above, once the ferrite grains are small enough and/or the MFZs are wide enough to lead to a depletion of carbon in the interiors of the α grains, the martensite-free α grains will be resulted. There is reason to believe that the pitting resistance of the duplex Femac-0.72C alloy can be noticeably improved as a result of the absence of the 18R martensite which is the most susceptible to the pitting attack. The obvious rise in the critical pitting potential of the duplex Femac-0.72C alloy shown in Figure 1 is reflective of such a change in the microstructure. The pitting initiation at the α/γ grain boundaries was followed by a sequence of the pitting attack inside the ferrite grains rather than the γ grains. This implies that the ferrite phase is more susceptible to the pitting corrosion than the austenite phase in the Femac alloy.

The present Femac alloys containing carbon contents ranging from 0.72 to 1.58 wt.% belong to the group of

the austenitic Femac alloys. They are called Austenitic since their microstructures essentially comprise a single-phase γ at solution heat treating temperature. In consequence of the absence of the ferrite phase and the α/γ grain boundaries with a higher energy than the γ/γ grain boundaries, the pitting corrosion resistance or the critical pitting potential can be further significantly increased, corresponding to the results shown in Figure 1. The alloys can be further subdivided into both with and without the κ' -carbides. By the formation of the fine κ' -carbides, the strength of these alloys can be greatly increased without significant loss in ductility. The existence of the fine κ' -carbides is thought to be beneficial to the mechanical properties of these alloys. On the other hand, the effect of the fine κ' -carbides on the pitting corrosion is evaluated in the present study. Based on the above experimental results for the Femac-0.93C and Femac-1.25C alloys, similar behaviors of the pitting attack could be observed regardless of the existence of the fine κ' -carbides. From the TEM analysis, the fine κ' -carbides having an ordered FCC structure of $L'1_2$ -type were formed within the austenite phase with a disordered FCC structure during quenching by spinodal decomposition, so that the rather low values of the coherent interfacial and strain energies between the fine κ' -carbide and the γ matrix would be resulted. It is thus to suggest that there is no detrimental effect of the existence of the fine κ' -carbides on the pitting corrosion resistance. This is consistent with the results obtained from the potentiodynamic polarization test shown in Figure 1.

Finally, the inclusions of manganese sulfide and aluminum oxide are frequently found in these Femac alloys since the manganese has a strong affinity to sulfur and the aluminum can be oxidized with much ease at smelting temperature about 1600°C. From the above examinations, the retained inclusions are responsible for the deterioration in the pitting resistance of the austenite phase. It is thus to believe that the pitting corrosion resistance will be further improved if the inclusions can be avoided to retained in the Femac alloy.

Conclusion

On the basis of the above observations, the pitting corrosion behaviors of the as-quenched Femac alloys with various carbon contents are strongly related to their microstructures. Some conclusions will be given below.

- (1) In martensitic Femac alloys, the interfaces between the martensites and the ferrite matrix provide much favorable sites for the pitting nucleation and the carbon content ranging from 0.06 to 0.61 wt.%. There is no obvious rise in the critical pitting potential as the 18R martensite is still present.
- (2) The pitting resistance of the duplex Femac alloy can be noticeably improved as a result of the absence of the 18R martensite which is the most susceptible to the pitting attack.
- (3) The α/γ grain boundaries as the substitutes for the 18R martensites to be the initiation sites for the pitting attack in the duplex Femac alloys.
- (4) Owing to the lower coherent interfacial and strain energies between the fine κ' -carbide and the austenite matrix, there is no detrimental effect of the existence of the fine κ' -carbides on the pitting corrosion resistance.

- (5) The retained inclusions of manganese sulfide and aluminum oxide are responsible for the deterioration in the pitting resistance of the austenite phase.

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Table I Chemical composition of the alloys

Alloy	Mn	Al	Cr	C	Fe	Structure
Femac-0.06C	30.4	8.63	3.51	0.06	Bal.	Ferrite + needle-like precipitates
Femac-0.32C	29.9	8.57	3.58	0.32	Bal.	Ferrite + Needle-like precipitates + Austenite
Femac-0.61C	29.5	8.61	3.54	0.61	Bal.	Ferrite + Needle-like precipitates + Austenite
Femac-0.72C	29.7	8.58	3.59	0.72	Bal.	Ferrite + Austenite
Femac-0.93C	28.4	8.50	3.50	0.93	Bal.	Austenite
Femac-1.25C	30.8	8.55	3.56	1.43	Bal.	Austenite + α'
Femac-1.59C	30.3	8.56	3.52	1.58	Bal.	Austenite + α'

Table II The Corrosion Data of Femac Alloys in 3.5% NaCl Solution

Alloy	E_{corr} (mV _{sce})	E_{pp} (mV _{sce})	I_{corr} (A/cm ²)	I_{pp} (A/cm ²)
Femac-0.06C	-312	-271	1.55×10^{-6}	4.98×10^{-6}
Femac-0.32C	-301	-267	8.28×10^{-7}	3.97×10^{-6}
Femac-0.61C	-299	-256	4.83×10^{-7}	2.73×10^{-6}
Femac-0.72C	-282	-201	3.28×10^{-7}	1.86×10^{-6}
Femac-0.93C	-273	-163	1.55×10^{-7}	8.40×10^{-7}
Femac-1.25C	-293	-158	1.92×10^{-7}	9.36×10^{-7}
Femac-1.59C	-295	-166	1.91×10^{-7}	8.82×10^{-7}

E_{corr} : Corrosion potential
 E_{pp} : Pitting potential
 I_{corr} : Corrosion current density
 I_{pp} : Breakdown pitting current density

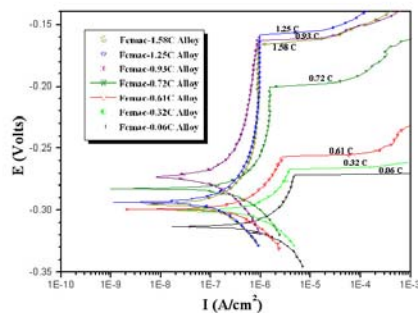


Figure 1. The potentiodynamic polarization curves for the present alloys with various carbon contents in 3.5% NaCl solution.

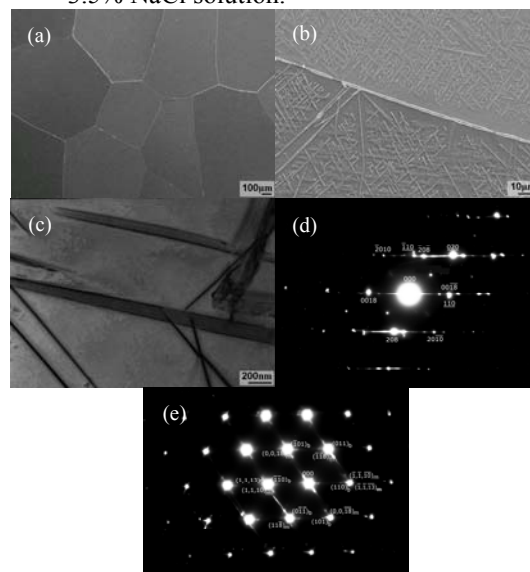


Figure 2. Electron micrographs of the as-quenched alloy A. (a)-(b) low and high magnification SEM micrographs, respectively. (c) TEM bright-field micrograph, (d)-(e) two selected-area diffraction patterns taken from a mixed region covering the needle-like precipitate and the ferrite matrix. The zone axes of the 18R martensite are [010] and [110], respectively. (m: 18R martensite, b: ferrite)

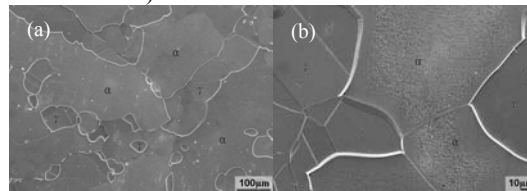


Figure 3. Electron micrographs of the as-quenched alloy B. (a)-(b) low and high magnification SEM micrographs, respectively.

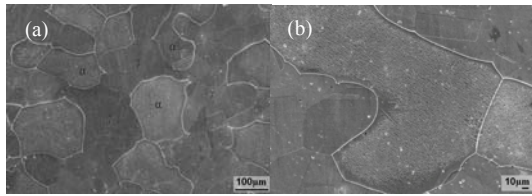


Figure 4. Electron micrographs of the as-quenched alloy C. (a)-(b) low and high magnification SEM micrographs, respectively.

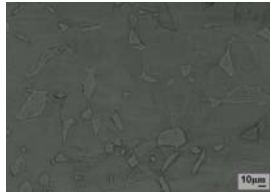


Figure 5. SEM micrograph of the as-quenched alloy D.

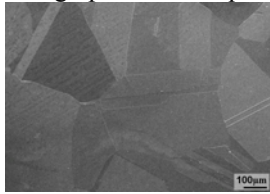


Figure 6. SEM micrograph of the as-quenched alloy E.

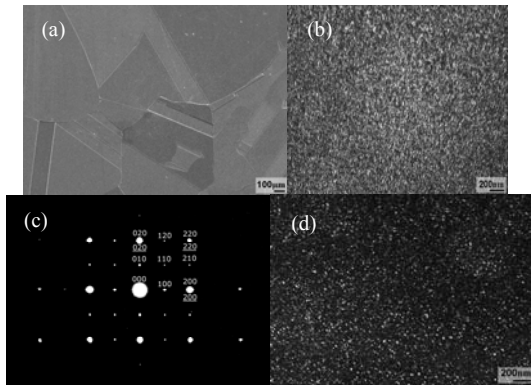


Figure 7. Electron micrographs of the as-quenched alloy F. (a) SEM micrograph, (b) TEM bright-field micrograph, (c) a selected-area diffraction pattern taken from a mixed region covering the austenite matrix and fine precipitates. The foil normal is [001] (hkl = austenite matrix; hkl = κ' -carbides). (d) 010 κ' -carbide dark-field micrograph

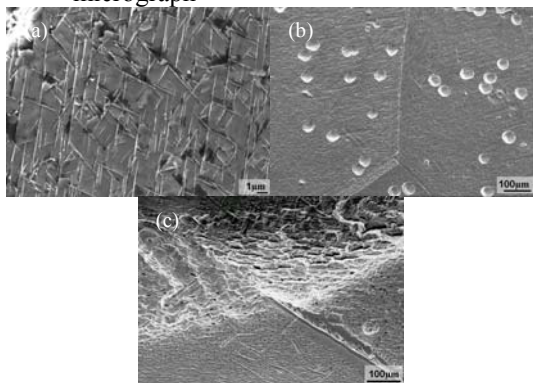


Figure 8. SEM micrograph of the as-quenched alloy A immersed in 6 wt.% FeCl_3 solution for (a) 5, (b) 20 minutes and (c) held at pitting potential in 3.5 wt.% NaCl solution for 10 minutes.

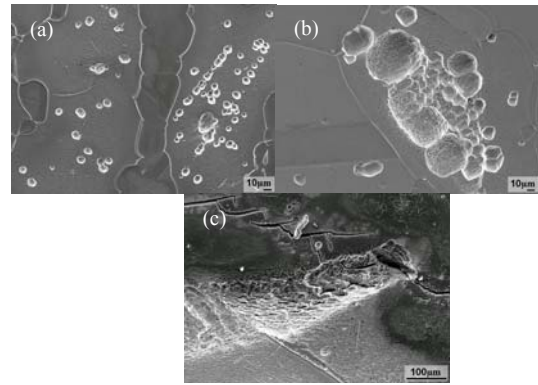


Figure 9. SEM micrograph of the as-quenched alloy B immersed in 6 wt.% FeCl_3 solution for (a) 35, (b) 70 minutes and (c) held at pitting potential in 3.5 wt.% NaCl solution for 15 minutes.

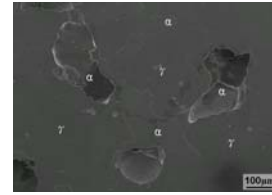


Figure 10. SEM micrograph of the as-quenched alloy C held at pitting potential in 3.5wt.% NaCl solution for 15 minutes.

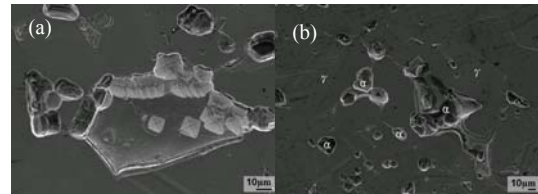


Figure 11. SEM micrograph of the as-quenched alloy D (a) immersed in 6 wt.% FeCl_3 solution for 60 minutes, (b) held at pitting potential in 3.5 wt.% NaCl solution for 20 minutes

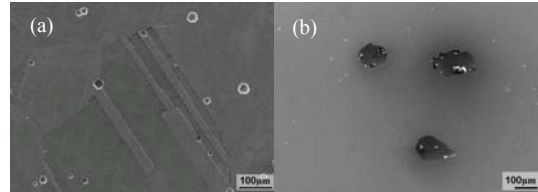


Figure 12. SEM micrograph of the as-quenched alloy E (a) immersed in 6 wt.% FeCl_3 solution for 120 minutes, (b) held at pitting potential in 3.5 wt.% NaCl solution for 45 minutes

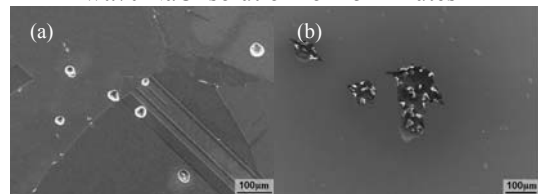


Figure 13. SEM micrograph of the as-quenched alloy F (a) immersed in 6 wt.% FeCl_3 solution for 120 minutes, (b) held at pitting potential in 3.5 wt.% NaCl solution for 45 minutes