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Corrosion and Passivation of Iron-Chromium Alloys

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Abstract

The corrosion and passivation of Fe-Cr alloys, heat-treated with different cycles, then subjected to different environmental conditions, were studied using metallographic, electrochemical and chemical techniques. On exposure of the thermally formed oxide films to air, for 8 months, the films formed on rapidly cooled specimens (Water Quenched, WQ) proved to be more protective than those formed on slowly cooled specimens (Furnace Cooled, FC). Potentiostatic polarization in sulfuric acid indicated that the rate of corrosion (current density) decreases with increase of Cr content, with a minimum value for the alloy 10 Cr. The grains varied in their susceptibility to attack. Some specimens were characterized by corrosion-resistant bands on the surface. The rate of passivation (current decay ratio) increased with increase of the temperature of heat-treatment and with an increase of Cr content for air cooled specimens (Air Cooled, AC). Thermal cycling lead to a decrease in the anodic current decay ratios. WQ specimens had lower current densities than FC or AC ones.

Spectrophometric analysis of the electrolyte after electrolysis indicated that Cr dissolved from FC specimens with higher rates than from WQ for the 5 Cr alloy, but for 20 Cr alloy, the reverse was true. The dissolved Cr increased with increase of Cr content for WQ while for AC specimens, no influence was seen. The dissolved metal ratio (Fe/Cr) had a maximum value at the alloy 10 Cr for WQ specimens, but for FC specimens this ratio decreased with Cr content of the alloy. However, if the heat-treatment cycle was repeated in FC type then the Fe/Cr ratio increased with increase of Cr content.

Introduction

Iron base alloys with varying contents of Cr and other elements, especially Ni, are used in a number of austenitic stainless steel articles, which are used mainly at high temperatures such as heat exchangers in the petrochemical industries, steam generators, ... etc. Although the environmental conditions are largely different in these applications, the materials in general change in their microstructure and composition. The interrelation between composition, microstructure, corrosion behavior, and mechanical properties of these materials has been the subject of numerous investigations¹⁻⁴. The importance of heat treatment of these steels on their behavior has also been recognized^{1,3}. However, the literature available on the effect of heat treatment upon various steels is not sufficient to

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resolve the controversies, and either conflicting results have been reported, or different interpretations have been given.

The present work was undertaken to gain further insight into this phenomenon.

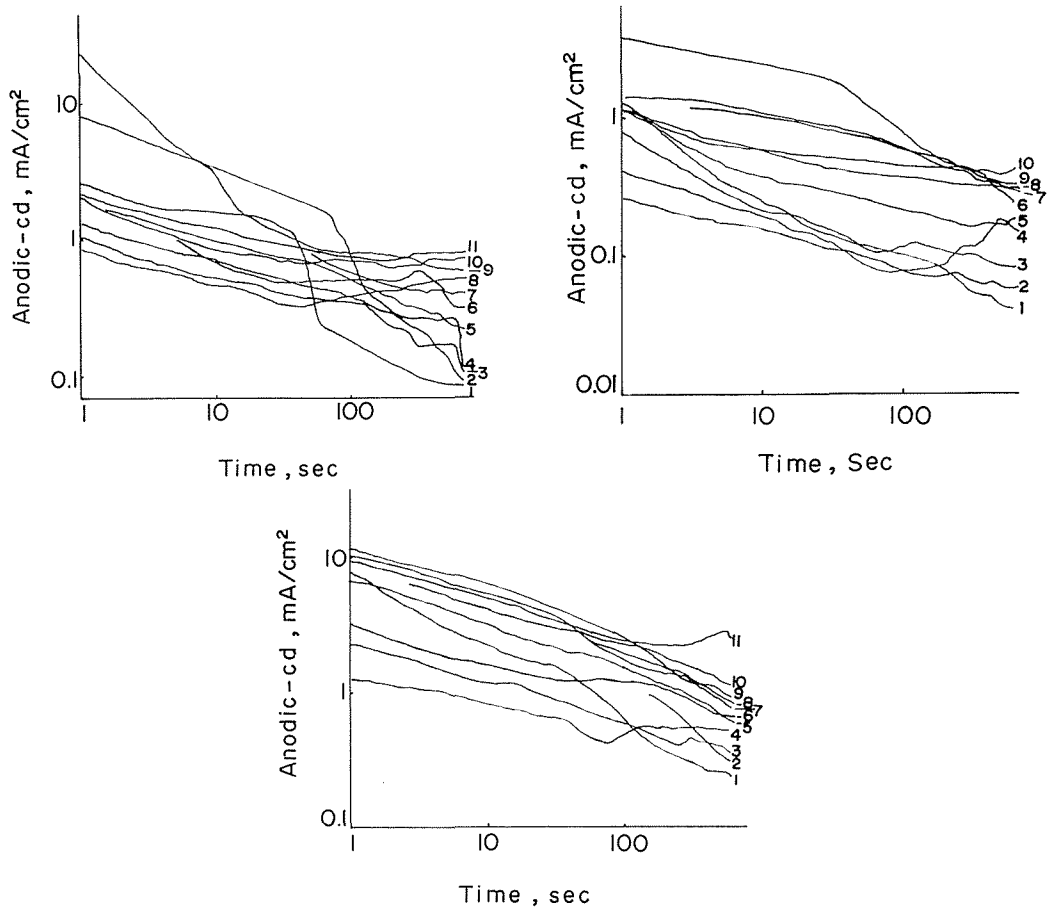
The alloying elements in steel are divided into two groups with respect to their effect on the α/γ equilibrium. Some of these elements stabilize the γ -phase and widen its single γ -phase field in the binary phase diagram. Others stabilize the α -phase and causes the so called γ -loop in the binary phase diagram²⁾. The role of Cr in the formation of alloys is more complicated. At high temperature, it is known to form a γ -loop while at lower contents the temperature range for the γ -phase is widened by a depression of A_3 temperature. The behavior of Cr was discussed in detail by Austin and Pierce⁵⁾, and they interpreted it in terms of the variation in the distribution coefficient of Cr between α and γ , depending upon the temperature and composition. Chromium is also known to be a ferrite stabilizer when added in high concentration. Further, no austenite is formed in alloys containing more than 14.3 at. % (13.4 wt%) Cr^{2,6)}. Thus the behavior of chromium changes with its concentrations: at low concentration it is an austenite stabilizer, whereas at high concentration it becomes a ferrite stabilizer and the phenomenon depends upon the negative value of the difference between the activity of chromium in γ and α -forms³⁾. The existence of variable phases in Fe-Cr system depends upon the heat-treatment cycle. Different phases of varying characteristics are produced by varying the chemical composition of ingredients. When Cr is added in a high concentration (e. g. 14 wt%) Cr-rich carbides and nitrides are formed instead of iron carbides and nitrides. Within a wide range the resulting changes in corrosion rates and morphology after corrosion attack by acids are analogous to the mechanical properties produced by thermal treatments of iron carbon alloys. Chromium depletion, occurring adjacent to chromium carbide precipitates, is generally considered to be the cause of intergranular attack in 18 Cr-8 Ni stainless steel which contains chromium carbide precipitates. Recent investigations^{7,8)} on Fe-Cr alloys are in agreement with such a hypothesis. Once, it was considered that the intergranular precipitated were iron carbides, which are readily soluble in acids⁹⁾, and thereby resulted in undercutting of the grains, or that chromium carbides and nitrides precipitated at grain boundaries surrounded by highly stressed metal which is dissolved more rapidly than unstressed metal¹⁰⁾, or that austenite formed at grain boundaries which is attacked preferentially due to its relatively low chromium and high carbon content compared with ferrite grains¹¹⁾. Chromium carbides and nitrides are formed in Fe-Cr alloys in the range 427-927°C, with a maximum near 799°C^{7,8)}. Rapid cooling rates from the treatment temperatures prevent the formation of these carbides. At very low concentrations of carbon, carbides are formed due to its precipitaton, which play an important role in the microstructure and anodic behavior of the alloys. The alloys with composition above the minimum of the γ -loop show different electrochemical and microstructural features, as compared with those of lower Cr contents.

Experimental

The compositions of the alloys used in this study are given in Table 1. Heat treatments were performed in a clean silica tube furnace under vacuum (10^{-3} Torr). They were cooled down to room temperature at different cooling rates. Thermally formed oxide films were investigated metallographically. The materials were, then, repolished and potentiostatically polarized in 0.1 N H_2SO_4 at 20°C and 600

Table 1 Chemical analysis of the alloys used in this study (wt)

| Alloy | Cr | Ni | Si | Mn | S | P | C | Cu | Co | Mo |
|-------|-------|-------|--------|-------|--------|-------|--------|-------|-------|-------|
| Fe | 0.001 | 0.04 | 0.008 | 0.005 | 0.0023 | | 0.0035 | 0.002 | | |
| 5 Cr | 4.90 | 0.001 | 0.0156 | 0.001 | 0.009 | 0.002 | 0.0043 | 0.01 | 0.02 | 0.001 |
| 10 Cr | 9.7 | 0.001 | 0.0074 | 0.001 | 0.011 | 0.002 | 0.0047 | 0.01 | 0.22 | 0.003 |
| 20 Cr | 19.4 | 0.001 | 0.0106 | 0.001 | | 0.002 | 0.0054 | 0.001 | 0.022 | 0.004 |
| Cr | 99.6 | 0.01 | 0.01 | | 0.03 | 0.005 | 0.02 | 0.005 | | |

**Fig. 1** Potentiostatic transient curves of anodic passivation of Fe-Cr alloys, 0.1N H₂SO₄, 600 mV, sec, 20°C:

- a) Fe-5 Cr: 1. 950°C, FC, 2 cycles, 2. as received, 3. 600°C, WQ, 4. 600°C, WQ+800°C, WQ, 5. 800°C, WQ, 6. 900°C, WQ, 7. 1,000°C, 30 sec, AC, 8. 1,000°C, 30 sec, AC: 4 cycles, 9. 800°C, FC+800°C, WQ, 10. 800°C, FC, 11. 1,000°C, 30 sec, AC: 2 cycles
- b) Fe-10 Cr: 1. 600°C, WQ, 2. 600°C, WQ+800°C, WQ, 3. 1,000°C, 30 sec, AC: 4 cycles, 4. 900°C, WQ, 5. 950°C, FC; 2 cycles, 6. as received, 7. 800°C, FC, 8. 800°C, WQ, 9. 800°C, FC+800°C, WQ, 10. 950°C, FC
- c) Fe-20 Cr: 1. 1,000°C, 30 sec, AC, 2. 1,000°C, 30 sec, AC: 2 cycles, 3. 1,000°C, 30 sec, AC: 4 cycles, 4. 600°C, WQ+800°C, WQ, 5. 800°C, FC, 6. as received, 7. 900°C, WQ, 8. 950°C, FC, 9. 800°C, FC, 10. 800°C, WQ, 11. 600°C, WQ

mV, sec. The electrochemical cell and electrical circuit has been described previously¹²⁻¹⁴. The potentiostatic transient curves of anodic passivation of Fe-Cr are of similar shapes (Fig. 1). Moreover, the current values after a certain time depend upon the alloy structure depending upon whether they consist of ferrite, austenite, or martensite and also on the composition of these phases. The potentiostatic transient anodic passivation is a comparative method. Consequently, the initial preparation of each specimen must be strictly identical. The specimens may be etched in potentiostatic conditions. When several phases are present, the dissolution of each phase occurs with a particular speed at a given potential. The experimental techniques and test methods are the same as those reported previously¹²⁻¹⁴.

Results

Different heat treatment cycles were applied to include all possible changes below or within the loop, and those that may occur in the solid state. The slow cooling rates after heat treatment at various temperatures facilitated the formation of carbides, whereas, high rate of cooling inhibited their formation.

During microscopic examination of the specimens it was observed that some of them are decorated by band formations. These bands are parallel to the surface and show geometrical shapes similar to scratching the surface with a knife. These bands were observed to occur even on the surface of the pure metals (Fe, Cr). When Fe-Cr alloys, oxidized during heat treatment, then exposed to air at ambient temperature for a prolonged period of 8 months it was proved that these types of bands were hardly affected by environmental conditions. Chemical attack by HNO_3 or by $\text{HF}/\text{H}_2\text{O}_2$ has only a slight effect on these bands. Recently, Streicher¹¹ mentioned the existence of crystallographically oriented fingers extending from the boundary into the grains. He also indicated that these fingers appeared

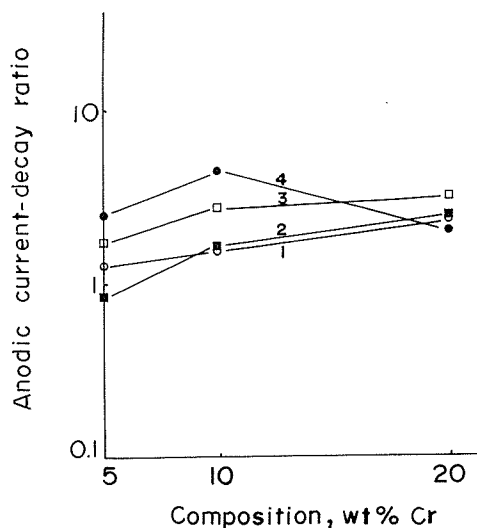


Fig. 2 Current decay ratio vs composition of Fe-Cr alloys:
 1. $I_{10\text{sec}}/I_{1000\text{sec}}$, 800°C, 1 h, FC, 2. $I_{1\text{min}}/I_{10\text{min}}$, 1,000°C, 30 sec, AC :
 4 cycles, 3. $I_{1\text{min}}/I_{10\text{min}}$, 800°C, FC+800°C, WQ, 4. $I_{10\text{sec}}/I_{1000\text{sec}}$,
 600°C, WQ

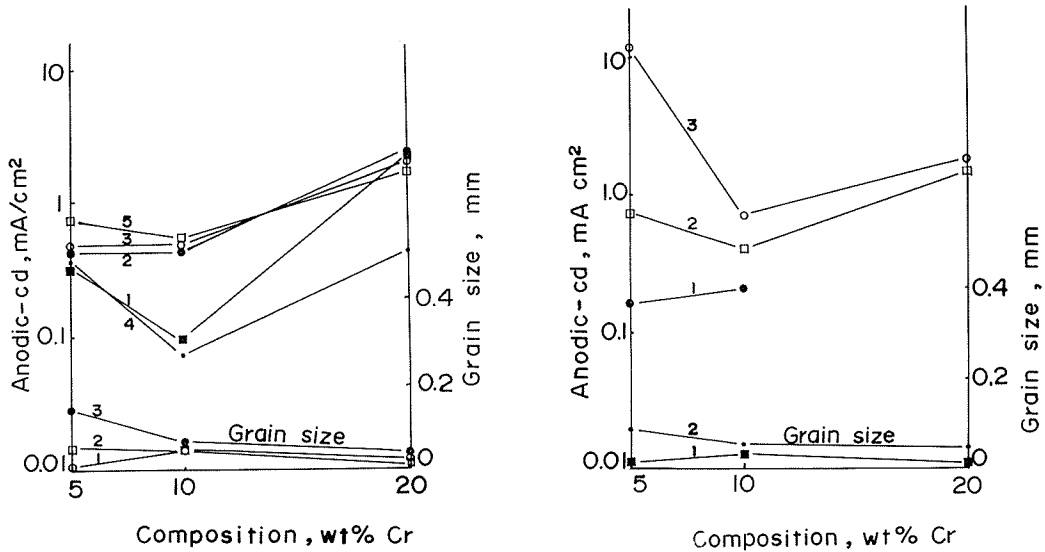


Fig. 3 Anodic current density vs composition of Fe-Cr alloys:

- a) 1. 600°C, WQ, 2. 800°C, WQ, 3. 900°C, WQ, 4. 600°C, WQ+800°C, WQ, 5. 800°C, FC,+800°C, WQ
 b) 1. 800°C, FC, 2. 950°C, FC: 2 cycles, 3. 950°C, FC

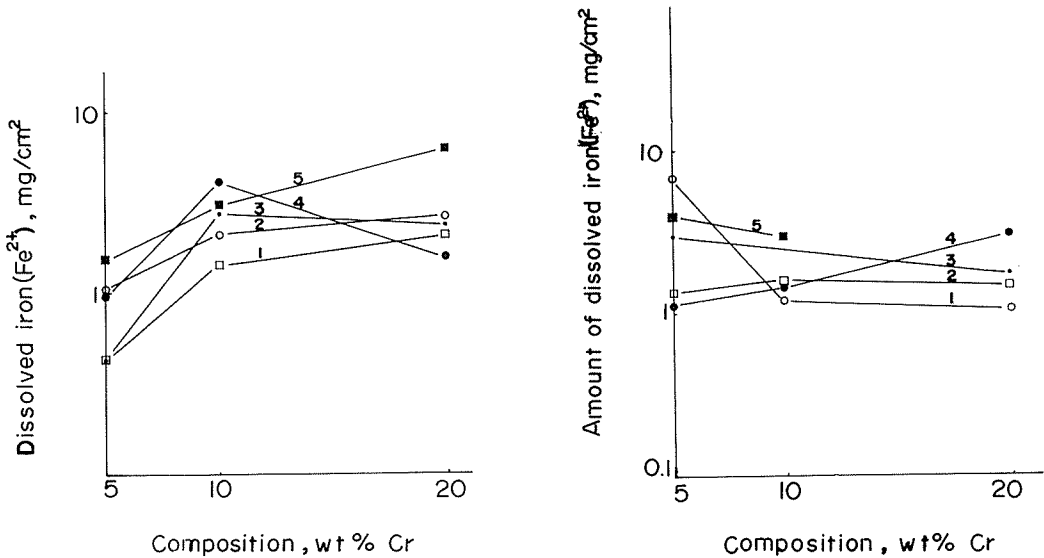


Fig. 4 Dissolved iron vs composition of Fe-Cr alloys:

- a) 1. 900°C, WQ, 2. 600°C, WQ+800°C, WQ, 3. 600°C, WQ, 4. 800°C, WQ, 5. 800°C, FC+800°C, WQ
 b) 1. 950°C, FC, 2. 1,000°C, 30 sec, AC: 4 cycles, 3. 1,000°C, 30 sec, AC: 4 cycles, 4. 800°C, FC, 5. 950°C, FC: 2 cycles

relatively free from intergranular attack, thus being a passive area. The potentiostatic transient curves of anodic passivation of Fe-Cr alloys shown in Fig. 1 clarify the relationship between the rate of passivation (rate of decay of current) and the thermal history of the specimen. The rate of decrease of anodic-cd increases with the decrease of Cr content. Accumulation of Cr corrosion products,

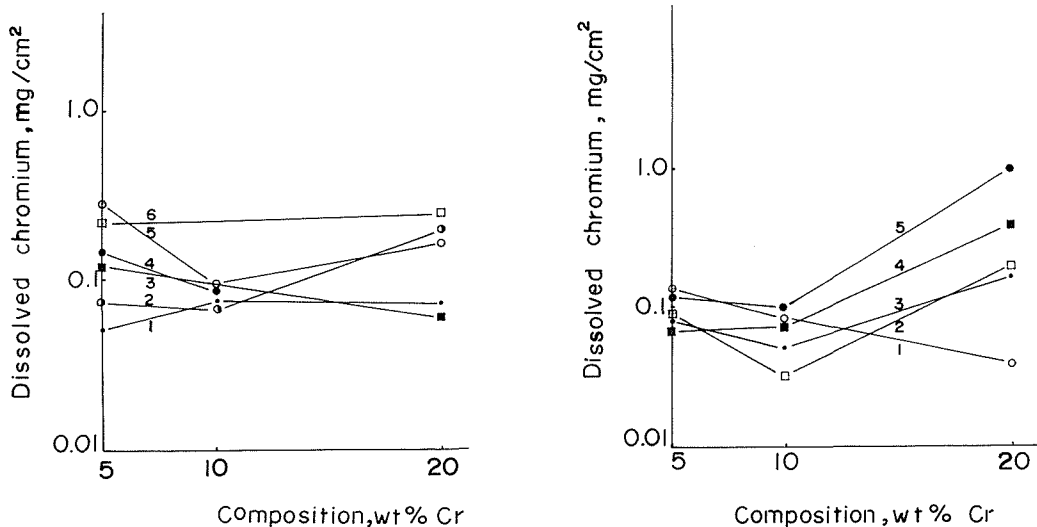


Fig. 5 Dissolved chromium vs composition of Fe-Cr alloys:
 a) 1. 1,000°C, 30 sec, AC: 4 cycles, 2. 800°C, FC, 3. 1,000°C, 30 sec, AC: 2 cycles, 4. 950°C, FC: 2 cycles, 5. 950°C, FC, 6. 1,000°C, 30 sec, AC
 b) 1. 800°C, WQ, 2. 900°C, WQ, 3. 600°C, WQ, 4. 600°C, WQ+800°C, WQ, 5. 800°C, FC+800°C, WQ

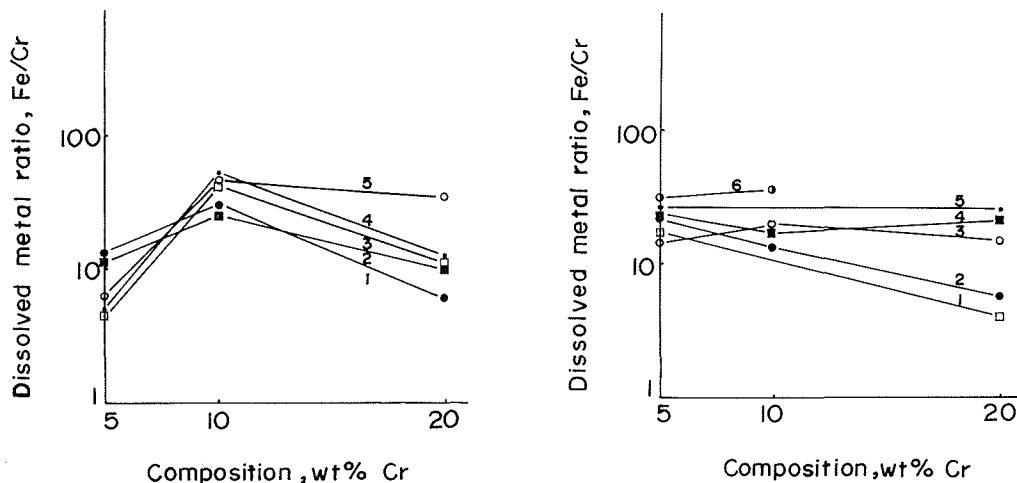


Fig. 6 Dissolved metal ratio, Fe/Cr vs composition of Fe-Cr alloys:
 a) 1. 800°C, FC+800°C, WQ, 2. 600°C, WQ+800°C, WQ, 3. 900°C, WQ, 4. 600°C, WQ, 5. 800°C, WQ
 b) 1. 1,000°C, 30 sec, AC, 2. 950°C, FC, 3. 800°C, FC, 4. 1,000°C, 30 sec, AC: 4 cycles, 5. 1,000°C, 30 sec, AC: 2 cycles, 6. 950°C, FC: 2 cycles

causes reactivation of Cr samples. Slowly cooled specimens (FC) show a stronger tendency to passivation as measured by the increase of relative current decay ratios indicated in Fig. 2. As the Cr content increases the tendency of passivation increases. When the heat treatment cycle is repeated several times followed by air cooling, then the nth cycle imparts a lower tendency to the passivation (lower current decay ratio). For rapidly cooled specimens (WQ) Cr contents do not

effect the corrosion of Fe-Cr alloys. Similarly, in this case, the sample bears no effect of the thermal cycling. The anodic-cd decreases to a minimum of 10 Cr alloy for both FC and WQ specimens (Fig. 3). The grain size and corrosion current of pure Fe and Cr are longer than in their alloys. The atomic absorption spectrophotometric analysis of the electrolyte, after electrolysis indicated that the WQ specimens have a lower tendency to corrode than the FC specimens. Thermal cycling in WQ increases the rate of iron dissolution while thermal cycling in air cooling (AC) decreases the amount of dissolved iron (Fig. 4). The dissolved Cr from WQ specimens largely increases with the increased Cr content, while Cr dissolved from slowly cooled specimens (FC, or AC) is not affected by Cr content of the bulk alloy or by repeated thermal cycles (Fig. 5). The relative amount of dissolved metals Fe/Cr decreases with the increase of Cr content for the slowly cooled specimens, while for WQ it is quite different since a maximum of this ratio exists at the 10 Cr alloy (Fig. 6). This indicated that Fe is easier to pass in solution leaving a Cr-enriched surface which gives more resistance against corrosion. The chemical attack of specimens with HF/H₂O₂ mixture showed that the creation and growth of pores is common for low Cr alloys (5 Cr) both around and inside of the grain boundaries, while the previously mentioned bands, are common for the alloys with a high content (20 Cr). The samples susceptible to intergranular attack are not passivated, and there is always the occurrence of active surface due to pore formation or deep grain boundary dissolution. In a typical grain boundary attack in 0.1 N H₂SO₄ (600 mV, sce) the boundary between corroded areas and the matrix is always smooth and can be observed by examining the surface of the specimen. The width of attacked zones (usually grain boundaries) increases with the increase of heat treatment temperature. In the corrosion in HF/H₂O₂ mixture the attack initiates and propagates along grain boundaries. It spreads further from the boundaries covering other areas and thus results in the formation of pores and large pits.

Discussion

The results of the present study are extended to the chromium-depletion theory of intergranular corrosion to ferritic stainless. The width of grain boundaries formed as a result of corrosion attack varied from one boundary to the other. This may be due to the differences in the orientation of the grains, because of different heat treatment procedures. The mixture of HF/H₂O₂ attacked all specimens at variable rates. The morphology of the attack of Fe-Cr alloys by HF/H₂O₂ is much different than that obtained by the treatment with H₂SO₄. It this may be due to localized corrosion, which was initiated because of the depletion in chromium after which the depleted zones were dissolved. In a strong oxidizing solution, the failure of the austenitic stainless steels may be associated with continuous grain boundary paths, which may be the results of secondary phase or of solute segregated regions¹⁵. The recovery of corrosion resistance by annealing at 800°C is due to the removal of stresses by heat treatment. The presence of visible chromium carbide precipitates in the microstructure provides evidence of the presence of chromium depleted zones, which accounts for the susceptibility of the specimen to intergranular attack both in oxidizing as well as in reducing environments¹¹. It is well known that the addition of Cr to Fe enhances the stability of passive film, provided that the Cr contents is not less than 12%¹⁶. The electron-diffraction results also showed that the substrate planes

either exhibit an epitaxial relationship with the oxide film or they lack the oxide diffraction spot patterns, or they show only diffraction rings³⁾. The low index substrate planes lose the orientation if the contents of Cr are low. For instance, the {100} plane no longer shows an epitaxially oriented oxide by the time the Cr contents reach 12%³⁾. On the other hand the high index planes, namely that is, the lesser atomic density planes, show greater relation of oriented oxide for high Cr contents, e. g., the {321} substrate has oriented oxide at 19% Cr. Strong diffraction rings were found only for the {110}, and orientation occurred in the alloys of 5% or 12% Cr contents. This observation described that the passive films on the {110} plane of Fe exhibited a greater tendency to disintegrate. The {110}, unlike the other orientations, had a different epitaxial relationship between the oxide and substrate depending on the passive or active state of the sample. McBee and Kruger³⁾ showed that the ring patterns found for the {110} are multiple and cannot be matched to the d-spacings for any of the Fe-Cr oxides. It was concluded that the addition of Cr to Fe may cause the polycrystallization of oxide films under natural conditions, and this accounts for their different behaviour. The passive films formed upon high Cr content alloys tends to be amorphous³⁾. More stable passivity or better corrosion resistance was encountered when Cr was added to Fe, which may be due to the presence of mixed oxides of Fe and Cr. Results of short period heating at 1,000°C and through various cycles support this view.

In conclusion, the present study of morphology of thermally formed surface films revealed that there is uniformity in the formation oxides with increasing concentration of Cr. For pure Fe and Cr surface modulations were observed after a short period of heating for 30 sec. at 1,000°C followed by air cooling (AC) in four cycles. In as much as pure Cr pitting was common for both furnace cooled (FC) and rapid cooling (WQ) specimens. In case of Fe-Cr alloys, thermal etching becomes evident and grain boundaries develop. The intensity of grain boundary oxidation increases with the increase in Cr content and temperature.

Exposure of thermally formed oxides to air for 8 months showed increased corrosion resistance with the increase of chromium content. WQ specimens have increased additional protective film compared with furnace cooled (FC) specimens. The extent of chemical attack by HNO₃ or by HF/H₂O₂ mixture shows that intergranular corrosion is usual for FC specimens. Pore formation is common in the alloys with low Cr contents (e. g., 5% Cr). Crystallographic dissolution occurred for FC pure metals at higher temperatures.

On the basis of above findings the main conclusions are as follows :

- 1) Current decay curves are of similar shape and a regular decrease occurs with time. Some of the specimens show a sharp decrease in current after 100 sec. Reactivation of specimens also takes place after passivation due to pore formation.

- 2) Current decay ratio increases with the increase in Cr content. Repetition of thermal cycles results in a decrease of this ratio, especially for AC specimens. The higher the temperature of heat treatment of FC specimens, the higher the value of this ratio (Fig. 2).

- 3) The current density as well as the grain size of Fe-Cr alloys is lower than that of individual pure metals. The alloy with 10% Cr has the lowest cd value.

- 4) The amount of dissolved iron increases with the increase in the Cr content. Alloys with 5-10% Cr have the lowest dissolution of iron, without being specific

to heat treatment cycles.

5) The amount of dissolved Cr during electrolysis is minimal for WQ specimens with 10% Cr. On the contrary dissolution of Cr is independent of its contents in case of FC or AC specimens. Repetition of heat treatment cycles reduces the amount of dissolved Cr from AC or FC specimens, while the reverse is true for WQ ones.

6) The dissolved metal ratio, Fe/Cr, is maximalum for WQ specimens, but it decreases with the increase in Cr contents in case of FC specimens.

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