Research Article

Contribution to the Study of the Relation between Microstructure and Electrochemical Behavior of Iron-Based FeCoC Ternary Alloys

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This work deals with the relation between microstructure and electrochemical behavior of four iron-based FeCoC ternary alloys. First, the arc-melted studied alloys were characterized using differential thermal analyses and scanning electron microscopy. The established solidification sequences of these alloys show the presence of two primary crystallization phases (δ(Fe) and graphite) as well as two univariante lines: peritectic L + δ(Fe) ↔ γ(Fe) and eutectic L ↔ γ(Fe) + Cgraphite. The ternary alloys were thereafter studied in nonde aerated solution of $10^{-3}$ M NaHCO$_3$ + $10^{-3}$ M Na$_2$SO$_4$, at 25°C, by means of the potentiodynamic technique. The results indicate that the corrosion resistance of the FeCoC alloys depends on the carbon amount and the morphology of the phases present in the studied alloys.

1. Introduction

Cobalt is one of the first transition series of elements. It lays between Fe and Ni and close to Cu in the periodic table. In nature, it shows a strong spatial association with these metals. Cobalt is a critical metal and it has many strategic and irreplaceable industrial uses (superalloys, magnets, corrosion- and wear-resistant alloys, high-speed steels, cemented carbides, diamond tool, etc.) [2–4]. Since cobalt shows great application potential, it has been widely studied.

This work is an academic study. It deals with the relation between the microstructure and electrochemical behavior of four iron-based FeCoC ternary alloys.

The solidification behavior of these alloys was studied in an earlier work [1]. This latter leads to the liquidus surface projection plot. In this paper, we undertake a study on electrochemical behavior of these alloys in nondeaerated solution of $10^{-3}$ M NaHCO$_3$ + $10^{-3}$ M Na$_2$SO$_4$, at 25°C.

2. Experiment

The studied alloys were arc melted in an argon gas atmosphere from pure elements (iron at 99.98 pct and cobalt at 99.5 pct from Aldrich Chemical Co.) and graphite. The solid-liquid and the solid-solid transformation temperatures were followed by a DTA-Netzsch 404S differential thermal analysis (cooling rate of 10 K/min) under argon atmosphere. The observation of the phases was performed using an optical microscope (ZEISSIM405) and a scanning electron microscope (SEM-JEOL).

The electrochemical tests were conducted using a Volta-LAB PGZ301 potentiostat. The corrosive medium consisted of neutral aqueous solution containing $10^{-3}$ M NaHCO$_3$ and $10^{-3}$ M Na$_2$SO$_4$. The polarisation curves are plotted in potentiodynamic mode. Potential was scanned from $-0.8$ V/SCE to $+1$ V/SCE in the direction of the increasing potentials at a scanning rate of 1 mV/s. Before each polarisation, the
3. Results and Discussion

In an earlier study [1], the compilation of the differential thermal analysis results in relation to the observed microstructures as well as the analysis of different phases allows us to establish the solidification paths of the studied alloys. Thus, the primary crystallization phases and the univariant reactions have been identified. The obtained results are summarized in Table 1. The proposed liquidus surface projection of Fe-Co-C system in the iron-rich corner, presented in Figure 1, shows, for the studied alloys, the presence of two primary crystallization phases (δ(Fe) and graphite) as well as two univariante lines: eutectic \( L \leftrightarrow \gamma(Fe) + C_{\text{graphite}} \) and peritectic \( L + \delta(Fe) \leftrightarrow \gamma(Fe) \). The studied alloys considered in this work are also shown in Figure 1 (encircled).

Potentiodynamic polarisation curves of the studied alloys in nondeaerated solution containing \( 10^{-3} \) M \( \text{NaHCO}_3 \) and \( 10^{-3} \) M \( \text{Na}_2\text{SO}_4 \) at 25°C are presented in Figure 2. The corresponding electrochemical parameters are given in Table 2.

We gathered in Table 3 corrosion current densities (\( i_{\text{cor}} \)) of the ternary FeCoC alloys with, respectively, the Fe/C ratio for each alloy. The results obtained for these alloys show that the corrosion current densities increase with the diminution of the Fe/C ratio.

Co6 and Co8 steels have a better corrosion resistance than Co3 and Co2 cast iron. This would be allotted to more important carbon content in cast iron.

The Co8 alloy corrosion current density is slightly lower than that of Co6. For these two alloys, the effect of carbon
Table 1: Compositions, transformation temperatures, and solidification sequences of FeCoC studied alloys. (*Temperature not detected by our differential thermal analysis apparatus limited to temperature lower than 1550°C).

| Alloy | Fe (wt. %) | Co (wt. %) | C (wt. %) | Temperatures/°C | Solidification sequences |
|------|-----------|------------|-----------|----------------|-------------------------|
| Co2  | 90.96     | 4.84       | 4.20      | *              | L ↔ C_{graphite}        |
|      |           |            |           | 1163           | L ↔ γ(Fe)               |
|      |           |            |           | 1150           | L ↔ γ(Fe) + C_{graphite}|
|      |           |            |           | 753            | Pearlite                |
|      |           |            |           | *              | L ↔ C_{graphite}        |
|      |           |            |           | 1170           | L ↔ γ(Fe)               |
|      |           |            |           | 1153           | L ↔ γ(Fe) + C_{graphite}|
|      |           |            |           | 763            | Pearlite                |
|      |           |            |           | 1496           | L ↔ δ(Fe)               |
|      |           |            |           | 1416           | L + δ(Fe) ↔ γ(Fe)       |
|      |           |            |           | 830            | γ(Fe) ↔ α(Fe)           |
|      |           |            |           | 756            | Pearlite                |
|      |           |            |           | 1477           | L ↔ δ(Fe)               |
|      |           |            |           | 1463           | L + δ(Fe) ↔ γ(Fe)       |
|      |           |            |           | 812            | γ(Fe) ↔ α(Fe)           |
|      |           |            |           | 772            | Pearlite                |
| Co3  | 89.37     | 6.50       | 4.13      | *              | L ↔ C_{graphite}        |
|      |           |            |           | 1170           | L ↔ γ(Fe)               |
|      |           |            |           | 1153           | L ↔ γ(Fe) + C_{graphite}|
|      |           |            |           | 763            | Pearlite                |
| Co6  | 90.90     | 8.45       | 0.65      | 1496           | L ↔ δ(Fe)               |
|      |           |            |           | 1416           | L + δ(Fe) ↔ γ(Fe)       |
|      |           |            |           | 830            | γ(Fe) ↔ α(Fe)           |
|      |           |            |           | 756            | Pearlite                |
| Co8  | 89.52     | 10.00      | 0.48      | 1463           | L + δ(Fe) ↔ γ(Fe)       |
|      |           |            |           | 812            | γ(Fe) ↔ α(Fe)           |
|      |           |            |           | 772            | Pearlite                |

Table 2: Electrochemical parameters of FeCoC ternary alloys corrosion (immersed in 10^{-3} M NaHCO₃ + 10^{-3} M Na₂SO₄, at 25°C).

| Alloy | E_{corr}/(mV/ECS) | i_{corr}/(μA/cm²) | R_p/(kΩ·cm²) | β_a/(mV/dec) | β_c/(mV/dec) |
|------|------------------|------------------|-------------|--------------|--------------|
| Co2  | −395             | 16.8             | 1.7         | 169          | −179         |
| Co3  | −390             | 18.2             | 1.3         | 99           | −178         |
| Co6  | −347             | 1.8              | 9.3         | 111          | −82          |
| Co8  | −337             | 1.7              | 9.8         | 110          | −88          |

Table 3: Variation of i_{corr} according to the Fe/C ratio.

| Alloy | Co8 | Co6 | Co2 | Co3 |
|------|-----|-----|-----|-----|
| i_{corr} (μA·cm⁻²) | 1.7 | 1.8 | 16.8 | 18.2 |
| Fe/C  | 186.5 | 184.5 | 21.66 | 21.64 |

and cobalt content does not appear. However, the microstructures of these alloys (Figures 3 and 4) present the same phases except that the pearlite structure is finer in Co6 alloy. This could explain the light increase of Co6 alloy corrosion current density.

In fact, it was reported that pearlitic structures corrode faster than spheroidized materials and steels containing fine pearlite corrode rapidly than those with coarse pearlite. In addition, the degree of dispersion of the carbide is quantitatively characterized by the total amount of interfacial contact between the ferrite and cementite phases [5–8].

In addition, Co2 alloy is more resistant than Co3 alloy in the experimental conditions of this study. The examination of the microstructures of these two samples (Figures 5 and 6) shows that the structure of carbon graphite is finer in Co3 alloy. This would lead to an increase of corrosion current density [9].

4. Conclusion

This work follows the study concerning the solidification behavior of iron-based FeCoC ternary alloys. The electrochemical behavior of some of these alloys is reported to solidification observed microstructures.

The results show the presence of two primary crystallization phases (δ(Fe) and graphite) as well as two univariante
2.5 kV \times 150 \mu m

Figure 6: Co3 electron micrograph showing graphite (1) and γFe/C eutectic (2).

lines: peritectic L + δ(Fe) \rightleftharpoons γ(Fe) and eutectic L \rightleftharpoons γ(Fe) + C_{graphite}.

The interpretation of the electrochemical results in relation with the observed microstructures leads to conclude that Co6 and Co8 steels have better corrosion resistant than Co2 and Co3 cast iron because of the more important carbon content in cast iron. Moreover, the corrosion current density increases with the decrease of in the Fe/C ratio. In addition, it was noted that the corrosion current density increases when the morphology is finer.

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