Carburization of Fe-Ni-Cr Alloys in CH₄-H₂ Atmospheres between 900 and 1100°C.

G. Matamala* and P. Cañete**

The corrosion behaviour of Incoloy 800 in Ar-CH₄-H₂ gas mixtures having a carbon activity of 0.95 was studied in the temperature range between 900 and 1100°C.

The kinetics, which can be described by the equation \((\Delta m/A)^2 = 2kt + c\), were determined gravimetrically. The k values obtained were 0.45, 1.24 and 5.99 (mg² cm⁻⁴ h⁻¹) at 900, 1000 and 1100°C respectively and the activation energy was determined to be 172 (kJ/mol). Both \(\text{M}_2\text{C}\) and \(\text{M}_7\text{C}_3\) carbides were observed, the former transforming to the latter upon an increase of carbon activity in the surrounding matrix.

INTRODUCTION

Carburization and metal dusting are corrosion problems experienced by high temperature alloys in industrial processes such as ethylene production, natural gas reforming, coal gasification, etc., which occur at temperatures higher than 700°C [1-3].

Our initial work in this area was carried out on iron [4-5], being extended now to the study of carburization of Incoloy 800 in Ar-CH₄-H₂ gas mixtures in the temperature range, 900-1100°C. The gas mixtures were relatively free of oxygen so that oxide formation [6-8] would not interfere with the carburization process.

Several authors [9-12] have reported on the kinetics and mechanisms of carburization of Fe-Cr, Cr-Ni and Fe-Cr-Ni alloys. The object of this work is to widen the study on the Incoloy 800 which is representative of Fe-Ni-Cr refractory alloys.

EXPERIMENTAL

The equipment used of the carburization experiments, described in detail in a previous paper [4], consisted of a Lindberg electric furnace with a digital temperature controller, a vitreosil reaction tube and two gas circuits. The weight gain of the samples was measured continuously by the extension of a fused silica spring using a cathetometer; the sensitivity of the measurement was 0.05 micrograms.

The Incoloy 800 specimens were of 10 x 10 x 3 mm dimensions, and their surfaces were finished to 600 grit by polishing. The composition of the alloy was Fe-32Ni-21Cr %wt.

The experiments were carried out by carburizing the samples in a Ar-CH₄-H₂ atmosphere with a carbon activity of 0.95. The reaction kinetics were determined at 900, 1000 and 1100°C for 200 hrs by measuring the weight gain of the specimens as a function of time.

The surface morphology of the samples was investigated by scanning electron microscopy. The progress of carburization was observed by metallographic techniques using Murakami’s reagent as etchant.

KINETICS RESULTS

Figure 1 shows the weight gain of the samples per unit area as a function of time. The weight gain begins after an incubation time, which was determined from a plot of the square of the weight gain per unit area versus time. This plot was a straight line at short times; the intersection of this straight line with the time axis gave incubation times of 110, 15 and 2 h at 900, 1000 and 1100°C respectively. This behaviour is consistent with the presence of a thin protective oxide layer on the alloy surface, which must be converted to a carbide layer by heating in the carburizing gas mixtures.

Fig. 1. Gravimetric measurements of the carburization of Incoloy 800 in Ar-CH₄-H₂ atmospheres at different temperatures \((a_c = 0.95)\).
Fig. 2 presents a plot of the square of the weight gain per unit area as a function of time from which the incubation period has been discounted. The resulting data followed initially an equation of the type:

\[
(\Delta m/A)^2 = 2kt + c
\]  

(1)

For longer times the data deviate from this equation, more so at higher temperatures, because the diffusion volume is progressively reduced as the carbon ingress takes place. This effect has also been observed by other workers [10, 11] and it is possible that such departure occurs when the two carburization fronts from opposing faces of the sample meet. Beyond this stage, a parabolic rate law would certainly not be expected since the boundary conditions have been altered.

Rate constants \( k \) obtained by linear regression analysis of the points in the straight line region of Fig. 2 are presented in Table I.

**TABLE I**

<table>
<thead>
<tr>
<th>( T )°C</th>
<th>( k ) (mg² cm⁻¹ h⁻¹)</th>
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</thead>
<tbody>
<tr>
<td>900</td>
<td>0.45</td>
</tr>
<tr>
<td>1000</td>
<td>1.24</td>
</tr>
<tr>
<td>1100</td>
<td>5.99</td>
</tr>
</tbody>
</table>

An Arrhenius plot of these \( k \) values is presented in Fig. 3, which includes the results obtained by Schnaas and Grabke who plotted \( 2k \) vs \( 1/T \) in their work [10]. The activation energy of 172 (kJ/mol) obtained in this work agrees well with that of Schnaas and Grabke of 167 (kJ/mol).

**DEVELOPMENT OF THE CARBURIZATION FRONT**

Fig. 4 presents a metallographic cross sectional view of the carburized samples exposed at 1000°C to an atmosphere of carbon activity of 0.95, at 6, 10, 50, 100 and 200 hours of carburization. Murakami’s reagent was used as etchant of the samples, after mechanical polishing.
The different structures observed, particularly in samples with 100 and 200 hours of carburization, are due to the precipitation of carbides of varying compositions [10]. The central area of the sample decreases in width when carburization time is increased, containing less $M_23C_6$ carbides.

According to Schnaas and Grabke [10] the $M_23C_6$ carbide contains increasing amounts of chromium as the carburization front progresses inwards; in regions of higher chromium the attack by the etchant is less as evident from Fig. 4.

The metallographic attack by Murakami's reagent permits the observation of an internal carburization front with $M_23C_6$ formation in the samples carburized for 6, 10 and 50 hours and a transformation front of carbides from $M_23C_6$ to $M_7C_6$ in samples carburized for 100 and 200 hours. The transformation reaction may be represented as,

$$w M_23C_6 + x C = y M_7C_6 + z M$$  \(2\)

From Fig. 4 it is possible to obtain kinetics data related to transformation front of $M_23C_6$ to $M_7C_6$ carbides.

<table>
<thead>
<tr>
<th>TABLE II</th>
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<tbody>
<tr>
<td>ADVANCE OF THE TRANSFORMATION FRONT OF CARBIDES AT 1000°C</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Time(s)</th>
<th>3.6 x 10^6</th>
<th>1.8 x 10^6</th>
<th>3.5 x 10^6</th>
<th>7.2 x 10^6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Position (cm²)</td>
<td>6.76 x 10^4</td>
<td>1.089 x 10^3</td>
<td>7.225 x 10^3</td>
<td>1.58 x 10^2</td>
</tr>
</tbody>
</table>

A linear regression of the data shown in Table II indicates a parabolic kinetic reaction with regression coefficient of 0.984 and a law which can be written as

$$\dot{\varepsilon} = D t + C$$  \(3\)

$$\dot{\varepsilon} = 2.355 \times 10^8 t - 1.438 \times 10^8$$  \(4\)

where $D$ represents the carbon diffusion coefficient in cm²/s, $\varepsilon$ is the advance of the transformation front of carbides in (cm) at time $t(s)$. The value of $D$ agrees well with that reported by Harrison and col. [11], for the 25 Cr-20 Ni-55 Fe alloy at 1000°C.

Fig. 5 shows the effect of temperature on the development and composition of the carburization front, in samples carburized for 200h. At 900°C the transformation front of carbides is at 0.34 mm from the surface. At 1000°C the carbide transformation interface is at 1.30 mm from the surface; the interface disappears at 1100°C, only coarser carbides of the $M_7C_6$ type being present at this higher temperature.

CARBIDE SURFACE MORPHOLOGY

Using scanning electron microscopy (SEM) it was possible to observe carbide nucleation on the alloy surface after carburization for different times. Fig. 6 presents photomicrographs taken by SEM on samples carburized in Ar-CH₃-H₂ gas mixtures of 0.95 carbon activity at 1000°C and for different times.

Thin particles of carbides of 1 μm size observed after 0.5h of carburization cover the major part of the sample surface. After 2h of carburization, the formation of a surface carbide layer is observed, which after 10h is totally continuous. After 50h, the continuous layer becomes porous. After 100h of carburization, the carbide layer develops into a discontinuous network.

The morphology of the surface carbide changes as the carburization temperature is changed. Figure 7 presents scanning electron micrographs of Incoloy 800 samples surfaces carburized for 200 hours at 900, 1000 and 1100°C. At 900°C the carbide surface is porous, with a distribution of needles. As the diffusion of carbon is facilitated by an increase of temperature, the carbide surface becomes progressively less porous. At 1100°C the carbides formed after 200 hours of carburization still have a compact structure which, due to carbon saturation at the edge of the sample is broken beginning the "metal dusting" process.

SUMMARY

The carburization of Incoloy 800 in Ar-CH₃-H₂ atmospheres follows a parabolic law at the beginning, deviating at longer times from parabolic behavior, presumably because of the hinderance to the diffusive flux of carbon provided by the precipitated carbides. Carburization is observed only after an incubation period which is shorter at higher temperatures.

The existence of this incubation period is probably related to the presence of a surface oxide film which blocks carburization in the initial stages.
FIGURE 6. SEM Micrographs of the surfaces of Incoloy 800 samples carburized at 1000°C and 0.95 carbon activity.
M_{23}C_6 carbides are formed first which later are transformed to M_{7}C_3 as the carbon activity increases. The transformation front progresses inwards as carburization proceeds, with a parabolic kinetic reaction law.

The carbide morphology at the alloy surface changes with temperature, becoming less porous as the temperature is increased.

ACKNOWLEDGEMENTS

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REFERENCES

5. G. Matamala: "Carburización de Fe, Ni y aleaciones Fe-Ni-Cr a altas temperaturas en atmósferas CH₄-H₂", Tesis de M. Sc., Universidad de Concepción, Chile (1982).