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Iron carburization in a calcium carbide molten salt solution

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The kinetics of iron carburization by both chemical and electrochemical treatments were determined at 920°C in a solution of CaC_2 in molten $CaCl_2$.

In order to study the mechanism of carburization, anodic and cathodic galvanostatic experiments were performed.

The iron carburization rate by chemical or anodic treatments was found to be controlled by the diffusion of carbon into the iron sample. Carburization rates under cathodic polarization are lower, and carburization may be prevented at the higher cathodic current densities. A mixed electrode model is proposed to explain the behaviour of the iron electrode in calcium carbide solutions.

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1. Introduction

It is well known that CaC_2 is soluble in molten halides [1] and CaC_2–$CaCl_2$ mixtures were used as electrolytes to study the anodic deposition of carbon [2] and to determine carbon activity in austenite [3].

More recently, a study on the galvanic cell Fe, C/CaC_2, $CaCl_2$/C has shown that austenite samples in contact with CaC_2 solutions undergo a carburization or decarburization reaction to reach an equilibrium value of carbon activity in austenite [4, 14].

CaC_2 solutions in molten salts could therefore be used instead of polluting cyanide baths for the carburization of steel [5]. This work has been performed in order to gain a better knowledge of this carburization process.

2. Experimental

Chemical and electrochemical treatments in CaC_2–$CaCl_2$ solutions were carried out at 920°C in an Inconel cell under argon atmospheres as described in a previous work [6]. Solutions of CaC_2 were prepared by dissolving technical grade CaC_2 in molten $CaCl_2$ which had previously been dehydrated by heating at 850°C under vacuum for 2 h in a graphite crucible.

Calcium carbide concentrations were determined by gas volumetric analysis of the acetylene evolved when samples of the bath were hydrolysed as described in a previous work [7].

Calcium oxide and free carbon were also present in the bath with a concentration of about 2% of CaO and 0·2% of fine carbon powder. Both components come partly from the technical calcium carbide used and partly by reaction of CaC_2 with the residual water existing in the bath after dehydration (about 0·1%).

Cylindrical ARMCO iron samples of 5 mm diameter were carburized by partial immersion in the bath to a depth of 4 or 5 cm.

The temperature of the bath (920°C) was such that the ferrite-austenite transformation occurred in a few minutes.

Electrochemical treatments were carried out by imposing different constant currents for various periods of time under cathodic or anodic polarization. The voltages between the iron sample and the graphite crucible were recorded as a function of time both in open circuit conditions during chemical treatments and under applied current during the electrochemical treatments.

After carburization, the samples were examined by metallographic techniques, and the carbon content determined measuring the volume of CO_2 evolved after complete combustion of the sample.

3. Results

The quantity of carbon which diffused into the samples as a function of time for the chemical, anodic and cathodic treatments respectively, is reported in Figs. 1, 2 and 3.

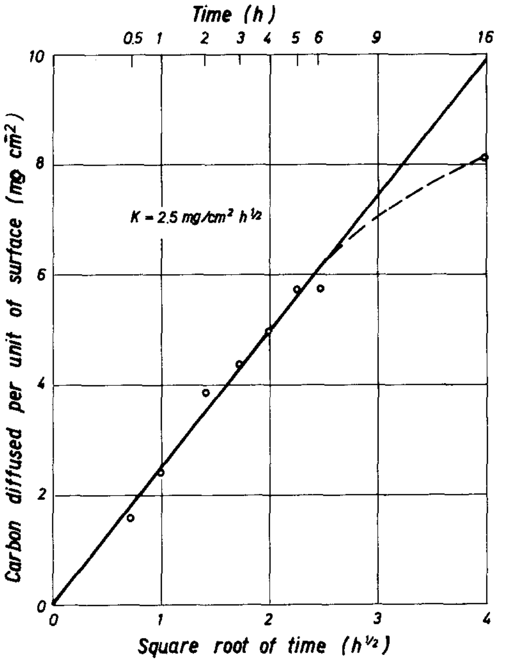

Fig. 1. Chemical iron carburization: carbon diffused as a function of time.

It can be observed that the plot of the quantity of carbon which diffused into the samples against the square root of time is approximately linear. The slopes obtained during anodic polarization runs are practically independent of the current density and are slightly higher than those obtained in the chemical treatments. Under cathodic polarization, the slopes obtained depend on current density and are smaller than in the case of the chemical or anodic treatments, especially at the highest current densities.

The treatments were carried out with two different bath compositions containing 4·7 and 6% of CaC_2. The same behaviour was observed for both baths.

Calcium oxide content was also different, ranging around 2%. The iron carburization process was apparently not influenced by the presence of a few percent of this component.

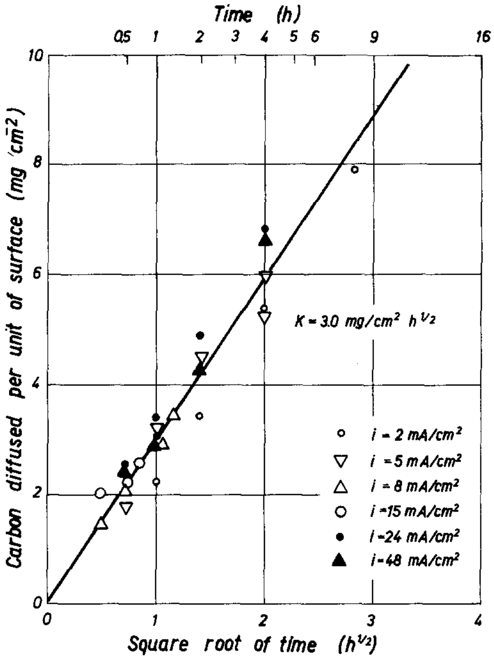

Fig. 2. Anodic iron carburization: carbon diffused as a function of time.

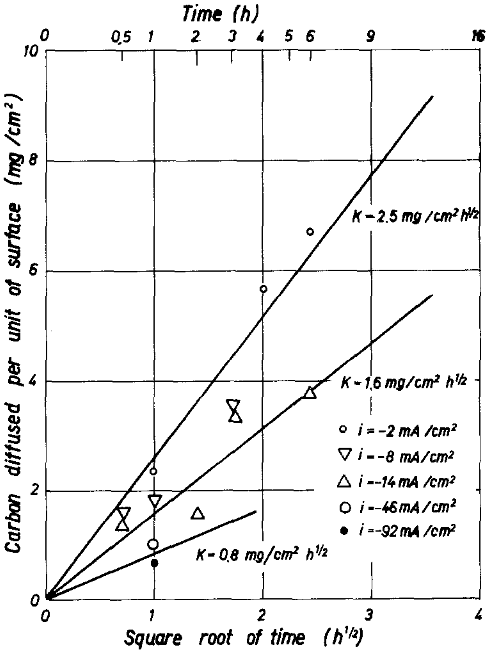

Fig. 3. Cathodic iron carburization: carbon diffused as a function of time.

Carbon deposits were obtained only after anodic treatments performed at the highest current densities (greater than 8 mA cm^{-2}) or at low

Table 1. Faraday efficiency for carbon discharge under anodic polarisation. Samples without external carbon deposit

Sample	*Current density* (mA cm^{-2})	*Time* (h)	*Theoretical carbon* (mg)	*Experimental carbon* (mg)	*Faraday efficiency*
F 18	1·95	2	12·1	23·8	1·97
F 19	1·99	1	6·05	15·0	2·48
F 20	1·95	4	24·2	37·2	1·54
F 5	4·82	1	14·5	20·3	1·40
F 7	4·82	0·5	7·25	11·9	1·64
F 12	8·75	0·25	6·05	9·30	1·54
F 13	7·95	0·5	12·1	14·9	1·23
F 14	14·8	0·25	11·0	13·6	1·23

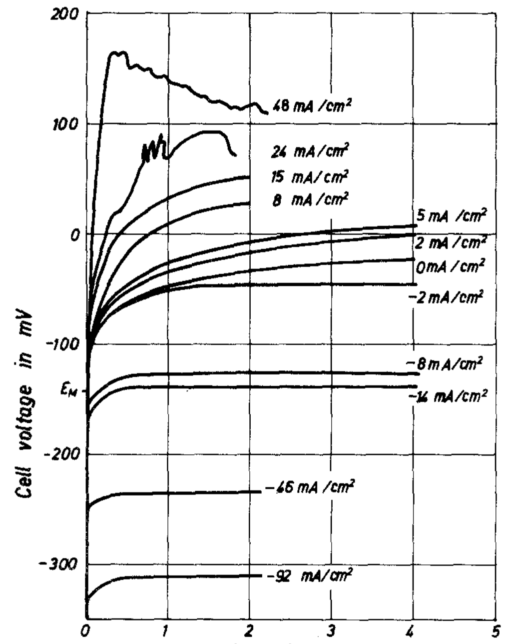

Fig. 4. Cell voltage as a function of time at constant current.

current densities after long periods of treatment (several hours).

In Fig. 4, the voltage of a cell consisting of the iron electrode and the graphite crucible (taken as reference) is reported as a function of time for chemical, anodic and cathodic treatments.

It may be observed that the open circuit potential of the iron electrode is about $-0{\cdot}15$ V at the beginning of the experiments, but shifts asymptotically towards zero during chemical treatments ($i = 0$). During anodic treatments ($i > 0$) the shift of the iron electrode potential is more rapid and may become positive with respect to the graphite crucible.

During cathodic treatments ($i < 0$), however, the potential drops suddenly at the beginning of the polarization, then increases slightly and maintains a constant level.

It must be noted that a carbon deposit on the iron electrode is observed at the end of the experiments during anodic treatments, only when the iron electrode becomes positive with respect to the graphite crucible.

Table 1 shows the Faraday Efficiency calculated on the basis of the carbon content analysis of the samples on the basis that carbon arises from the anodic discharge:

$$[(C_2^{2-})]_{\mathrm{CaCl_2}} \longrightarrow 2\langle \mathrm{C}\rangle_{\mathrm{Fe}} + 2e^-$$

produced by the external anodic current imposed. We found that the Faraday Efficiency was greater than 1 when the samples were treated anodically under conditions which did not produce an external carbon deposit. The highest Faraday Efficiency values were obtained for samples treated at the lowest current densities for short periods of time.

Five samples on which there was a carbon deposit have also been analysed by determining both the diffused and deposited carbon (Table 2). The values are rather scattered although most of them are less than unity. A possible source of error is the detachment of deposited carbon during the extraction of the samples from the cell. The deposited carbon does not adhere well to the metal. In any case, the values obtained are closer to unity than those reported in Table 1 for samples free from carbon deposits.

Table 2. Faraday efficiency for carbon discharge under anodic polarisation. Samples with external carbon deposit

Sample	*Current density* ($mA\,cm^{-2}$)	*Time* (h)	*Theoretical carbon* (mg)	*Experimental carbon* (mg)	*Faraday efficiency*
F 6	5·17	4	58·0	37·7	0·65
F 11	7·77	1	24·2	25·4	1·05
F 15	14·5	0·5	22·0	21·8	0·99
F 16	14·2	0·75	33·0	27·1	0·82
F 17	14·5	1	44·0	37·4	0·85

4. Discussion

Our results show that when pure iron in the austenite phase comes in contact with a molten solution of CaC_2 in $CaCl_2$, the following carburization reaction occurs:

$$[(CaC_2)]_{CaCl_2} \longrightarrow 2\langle C\rangle_{Fe} + [(Ca)]_{CaCl_2}. \quad (1)$$

The occurrence of this reaction could be taken into account simply by considering that the CaC_2 solution was equilibrated with pure graphite. Therefore, for purely thermodynamic reasons, it was expected that the iron sample with a carbon activity lower than unity, dipped into the bath, would become saturated with carbon.

The Reaction 1 is actually governed by the equilibrium:

$$[(CaC_2)]_{CaCl_2} \rightleftharpoons [(Ca)]_{CaCl_2} + 2\langle C\rangle_{Fe} \quad (2)$$

and the extent of the carburization reaction depends therefore on the level of the calcium activity in the bath. The carburization reaction observed proceeds as a consequence of the fact that calcium formed near the surface of iron can diffuse into the bath probably more rapidly than carbon into iron. The large volume of the bath with respect to the quantity of calcium formed by Reaction 1 avoids practically any sensible increase of calcium activity in the bath.

The equilibrium constant of Reaction 2 calculated from the free energy of CaC_2 [13] is of the order of $1{\cdot}0 \times 10^{-4}$ at 920°C.

If the chemical Reaction 1 is a fast one and if we can exclude the possibility of the diffusion of carbon bearing species in the melt as a rate-determining step for the carburization reaction, the fact that the quantity of carbon diffused into the samples is a linear function of the square root of time indicates that the process is probably controlled by the diffusion rate of carbon into the iron samples.

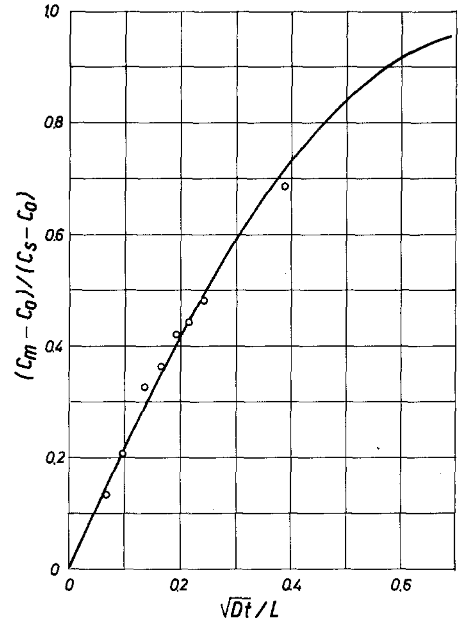

Fig. 5. Chemical iron carburization: agreement between theoretical diffusion curve and experimental results.

In the case of cylindrical diffusion, the diffusion theory [8] gives a solution which has been plotted as a solid line in the diagrams of Figs. 5, 6 and 7 containing the two non-dimensional parameters: $(C_m - C_0)/(C_s - C_0)$ and $\sqrt{(Dt)}/L$, where C_m is the average concentration of the diffusing species in the samples, C_0 the initial concentration, C_s the surface concentration, D the diffusion coefficient, t the time of diffusion and L the radius of the cylinder.

In order to calculate the non-dimensional parameters, we have used a diffusion coefficient

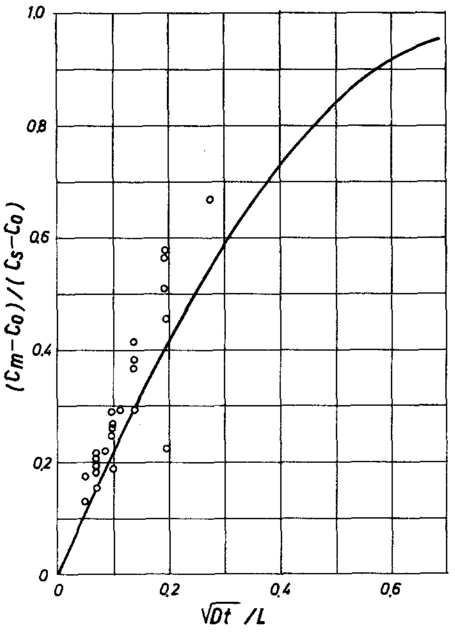

Fig. 6. Anodic iron carburization: agreement between theoretical diffusion curve and experimental results.

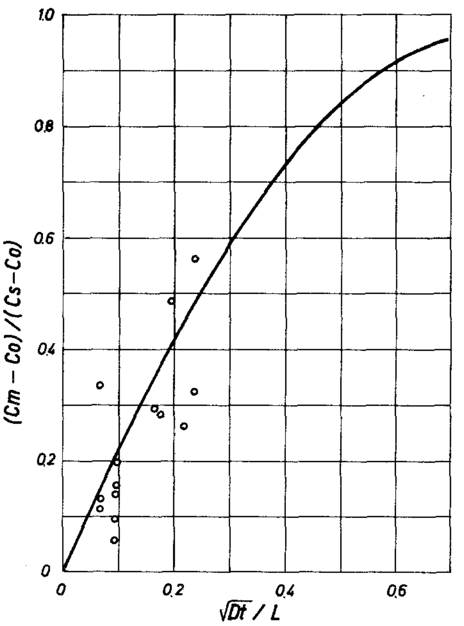

Fig. 7. Cathodic iron carburization: agreement between theoretical diffusion curve and experimental results.

of carbon in iron [9] equal to $1{\cdot}657 \times 10^{-7}\,\mathrm{cm}^2\,\mathrm{s}^{-1}$ at 920°C. For the surface concentration C_s, as we do not know the actual surface value, we have assumed that the surface of the iron is saturated with carbon, thus a value of 1·25% of carbon can be obtained from the Fe–C phase diagram at 920°C [10]. The average concentration C_m is that obtained by carbon analysis of the samples, and the initial concentration C_0 is considered zero for ARMCO iron. The agreement existing between the theoretical diffusion curve and the experimental points may be verified in Figs. 3, 6 and 7 for chemical, anodic and cathodic carburization respectively. The chemical carburization closely agrees with the theoretical curve. For anodic carburization, the experimental points are more scattered and are higher than the theoretical curve. Cathodic treatments give much more dispersed points and most of these values are lower than those corresponding to the theoretical curve.

For anodic treatments, we can explain this deviation by assuming that the surface of iron may be supersaturated in carbon to a slight extent. Under this condition, C_s will be slightly higher, the ratio C_m/C_s slightly lower, and the calculated points will be above the theoretical curve.

In the case of cathodic treatments, the establishment of surface concentrations of carbon lower than the saturation value explains the lower carburization rates observed experimentally.

The fact that the carburization rate is influenced by the applied cathodic current indicates that the mechanism of carburization may be of an electrochemical nature. Moreover, the deviations from Faraday's Law observed for the carbon discharge under anodic conditions may be characteristic of the presence of a mixed electrode process during the chemical carburization of the iron samples.

We can propose reasonably that at the iron electrode, the carburization reaction occurs as a mixed electrode process with the occurrence of the anodic reaction:

$$[(C_2^{2-})] \longrightarrow 2\langle C\rangle_{Fe} + 2e^- \qquad (3)$$

and the cathodic reaction:

$$[(Ca^{2+})] + 2e^- \longrightarrow [(Ca)] \qquad (4)$$

supposing that calcium carbide is at least partially dissociated as some authors have shown [1, 15].

Under these conditions, the iron electrode will take up a mixed potential depending on the current-potential behaviour of a carbon and a calcium electrode corresponding to the respective electrode Reactions 3 and 4.

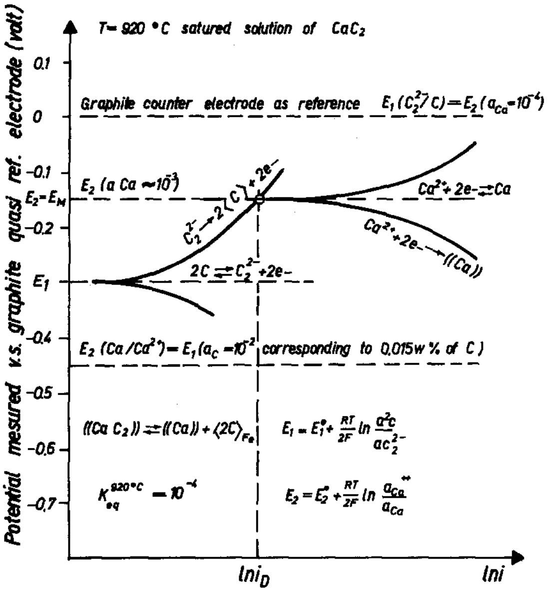

Fig. 8. Proposed mixed potential model for iron electrode in a calcium carbide molten salt solution.

Actually a calcium electrode will probably have a much higher exchange current than a carbon electrode. In fact, liquid metal electrodes in molten salts have the highest exchange currents known in electrochemistry [11]. As a consequence, the situation arising at the iron electrode dipped in a calcium carbide solution in molten $CaCl_2$ can be represented by the Evans diagram shown in Fig. 8. Under this condition, the iron electrode takes up a mixed potential corresponding to the potential of a calcium electrode as in fact previous authors have observed [4].

Despite the fact that we have not used a graphite reference electrode, we can nevertheless consider the potential of our graphite counter electrode to be reasonably close to that of a graphite reference electrode. In fact, during cathodic treatments. we have an anodic polarization of the counter electrode, but considering the low current densities used and the large surface area of the counter electrode, its potential will be close to that of a graphite reference electrode.

In the case of the anodic treatments calcium ions are presumably discharged on the counter electrode, but this discharge leads probably to the formation of CaC_2 as the final product. The formation of CaC_2 by electrolysis of molten calcium halides on a graphite cathode is reported in the literature [16].

In other words, our graphite counter electrode acts as a buffer keeping the activity of calcium metal near the value corresponding to the reaction equilibrium:

$$[(CaC_2)]_{CaCl_2} \longrightarrow \langle C\rangle_{graphite} + [(Ca)]_{CaCl_2}. \qquad (5)$$

As a consequence, considering the low current densities used, we suppose that the potential of our counter electrode will always be rather close to the potential of a graphite reference electrode.

Assuming a mechanism of carburization as described above and taking the potential of our graphite counter electrode as the reference potential, we can explain the cell behaviour observed during chemical, anodic and cathodic treatments in a semi-quantitative manner as follows.

An iron electrode dipped in a calcium carbide solution in the absence of polarization will be carburized in the first minutes of immersion at a very high rate because the diffusion of carbon into the iron sample is very fast under these conditions. Consequently, large quantities of calcium will be formed by Reaction 1, and the iron electrode will take up a relatively high negative potential. As the carburization continues, the diffusion rate slows down and as a consequence, calcium is produced in smaller quantities. Its activity near the electrode will be reduced and the potential will shift asymptotically from negative values to zero, as can be observed in Fig. 4 for the curve corresponding to $i = 0$.

It must be remarked that in the first minutes of iron sample carburization, the presence of a high activity of calcium near the electrode hinders, as a consequence of Equilibrium 2, the establishment of conditions of carbon saturation on the iron surface. In fact, we have recorded a starting potential of about −0·15 V. This corresponds to a calcium activity of about 10^{-3}, which is ten times higher than the thermodynamic activity corresponding to carbon saturation of iron. This potential (and, as a consequence, the calcium activity) rapidly decreases, and conditions that are near the carbon saturation are reached on the iron surface. This short period of time at lower values than carbon saturation values on the surface has practically no influence on the total diffused as we can see in Fig. 5, where a good agreement exists between our experimental points and the theoretical diffusion curve.

When a constant anodic current is imposed, Ca formation rate of Reaction 4 decreases as does the Ca activity near the electrode, this will be lower than in the case of chemical carburization. The iron electrode potential will then increase more rapidly and eventually reach values higher than the zero reference when the carbon deposit occurs, depending on the overpotential of the discharge reaction of C_2^{2-} to form a carbon deposit. This can be seen in Fig. 4 for $i > 0$. The irregular cell voltage behaviour which may be observed at the higher anodic currents in Fig. 4 is probably due to the disordered growth of the carbon deposit.

When a constant cathodic current is imposed, the Ca formation rate of Reaction 4 increases and the Ca activity near the iron sample will be higher than in the case of chemical carburization. Subsequently, lower surface concentrations of carbon will be present according to Equilibrium 2, and carbon will diffuse at lower rates. The potential of the iron electrode will decrease as a consequence of the higher Ca activity existing near the electrode. Because the cathodic current applied is constant and the counterdiffusion process of Ca into the solution reaches steady state conditions after a certain time, it may be expected that the Ca activity near the electrode surface, and consequently the electrode potential, will also reach a constant value after a certain time as in fact can be seen in Fig. 4 for $i < 0$.

If the cathodic current is sufficiently high, we may expect to have a Ca activity near unity in the neighbourhood of the electrode. In this case, the carbon activity on the iron surface will be about 10^{-2} which corresponds to 0·015% of carbon (Ban-Ya, Elliot and Chipman Equation) [12]. This situation should arise at about −0·45 V with respect to the graphite reference electrode. Actually we never reached these levels in our treatments. For a cathodic current of 92 mA cm^{-2} we recorded a potential of −0·31 V as we can see from Fig. 4. In fact, the sample treated under this condition still showed a very slight carburization.

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