Experimental and Numerical Study of C Electromigration in Iron During Ferrite-to-Austenite Transformation



PATRICE CHANTRENNE, MAXIME MONZEY, DAMIEN FABRÈGUE, PIERRE-ANTOINE GESLIN, MICHEL PEREZ, and FLORIAN MERCIER

The influence of the electric current on the diffusion of carbon in an ARMCO iron sample is studied. The sample, placed between two graphite punches, is heated in the intercritical domain (between 736 °C and 912 °C) thanks to Joule heating. The diffusion of C in ferrite induces its transformation into austenite. After cooling, the microstructure of the sample gives information on the transformation fronts positions and C concentration profiles. The transformation front velocity is higher in the direction of the electric current and lower in the opposite direction. To understand and predict this phenomenon, a new model accounting both for the allotropic phase change and the electromigration of C in iron is proposed. Some model parameters are fitted comparing the predicted and the measured interface positions. With these parameters, the simulated C concentration profile is in good agreement with the experimental one.

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I. INTRODUCTION

HEAT treatments are key processes in metallurgy to tune the microstructure and the resultant mechanical properties for a given application. Conventional thermal treatments are done using radiative and convective heat transfer. They are very time- and energy-consuming. Joule heating (induction heating, Spark Plasma Sintering, etc.) is an interesting alternative method; it includes alternating, direct, continuous and pulsed currents (a.k.a. electropulsing (EP)). Induction furnaces allow fast heating rate (over 100 °C/s) and low thermal inertia. Until recently, thermal treatments assisted by electric current were considered equivalent to conventional heating methods. However, spectacular enhanced kinetics induced by Joule heating have been reported for intermetallic compound growth,^[1] phase recrystalliza-tion^[2] and microstructure changes.^[3] Several works^[4–6] suggest that these phenomena might be due to either the enhancement of defects mobility or the modification of the system Gibbs free energy modification. The

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interpretation of experimental observations is difficult, mainly because the experimental conditions do not always allow to distinguish the influence of the electric current and the temperature level due to Joule heating. Nevertheless, it is now clear that the electric current has a significant influence on the microstructure evolution in metals and alloys. All the physical phenomena induced by electric current are not fully understood, especially when phase change occurs. However, it opens new routes to tailor new microstructures and to improve the process productivity. Moreover, thanks to the direct Joule heating but also because the electric current allows decreasing the temperature level of thermal treatment, the energy consumption is significantly reduced.

Electromigration (EMG) is a mechanism of mass transfer observed in metals crossed by high electric current densities. In 1861, Gerardin was the first to report observations of this phenomenon as he described the motion of atoms in molten salts under an applied voltage.^[7] As might be expected, EMG in solid metals takes place at a much slower rate than in liquid metals. Consequently, for a number of years it was thought that the effect did not occur in solid metals. However, in the early 1930s a number of investigators experimentally demonstrated EMG in solid metals by using sufficiently high current densities and temperatures. Skaupy introduced in 1914 the concept of "electron wind",^[g] which laid the foundation for the understanding of EMG. The electrons flow through a metal submitted to an electric current and collide with metal atoms, resulting in momentum transfer. In the 1950s, Seith and Wever

PATRICE CHANTRENNE, MAXIME MONZEY, DAMIEN FABRÈGUE, PIERRE-ANTOINE GESLIN, MICHEL PEREZ, and FLORIAN MERCIER are with the Univ. Lyon, INSA-Lyon, Université Claude Bernard Lyon 1, CNRS, MATEIS, UMR 5510, 69621 Villeurbanne, France. Contact e-mail: patrice.chantrenne@insalyon.fr

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Fig. 1—(a) Plot of effective charge of carbon in ferrite Z_{α}^* vs temperature *T*, at different electric current densities (represented with a heatmap color scale). (b) Plot of effective charge of carbon in austenite Z_{γ}^* vs electric current density (100 to 3000 A/cm²), at different temperature levels (represented with a heatmap color scale). Data from Okabe *et al.*,^[12,13] Nakajima *et al.*,^[14,15] Falquero and Youdelis.^[16] (Color figure online).

presented the first systematic studies of EMG based on the correlation between the direction of the current flow and the material transport.^[9] Fiks^[10] and Huntington and Grone^[11] both proposed the first mathematical formulations of the driving force of EMG:

$$\vec{F} = e\vec{E}Z^*$$
[1]

where *e* is the charge of an electron, \vec{E} is the electric field intensity and Z^* is the effective charge of metal atoms. The latter is one of the most important quantity to evaluate the magnitude of electromigration, as it sets the amplitude of the driving force which is the sum of the direct electrostatic force and the electron wind force. Consequently, a drift velocity, \vec{v}_d , originates from this force and leads to a mass transfer in the direction of the electric field.

The increasing presence of Joule heating in the steel industry motivates the study of the effect of electric current in iron, ferrous alloys and steels. Most thermal treatments of these materials imply heating in the intercritical domain, in which the increase of C concentration leads to the phase transformation of ferrite into austenite. Among the different metallurgical processes, solid (pack) carburizing is used to easily increase the C content and the surface hardness of iron or steel. It is a heat treatment process in which the ferrous material absorbs C while the metal is heated in the presence of a carbon-bearing material such as charcoal or carbon monoxide. Thus, it is of utmost importance to study the electromigration of C in both iron phases and the possible influence of the electric current on phase transformation kinetics. However, few data are found in the literature about electromigration of C in iron or carbon steels, and only for single phase materials (ferrite or austenite). The effective charge of C in single phase (α or γ) iron was experimentally determined many years ago by Okabe and Guy,^[12,13] Nakajima *et al*.^[14,15] and Falquero and Youdelis.^[16] They used the steady-state method to determine its value in either ferrite or austenite, at several temperature levels and electric current densities. Nakajima et al.^[15] determined the equivalent charge of C in ferrite, Z_{α}^{*} , (Figure 1(a)) for temperatures between 550 °C and 850 °C and for current densities between 100 and 900 A/cm². Its value drops from + 12.2 at 550 °C to + 3.5 at 850 °C. For temperatures higher than 700 °C, Z_{α}^* scatters between + 3 and + 4. The uncertainty on the data values is ± 0.5 because of the small influence of electric current density on Z_{α}^* . The effective charge of C in austenite, Z_{α}^* , at different electric current densities have also been measured for temperatures between 920 °C and 1000 °C (Figure 1(b)). Its value significantly depends on electric current density, dropping from + 14 for low current densities to values around + 4 for high current densities. The effect of the temperature level is not clear and a single value of Z_{γ}^* is reported in the intercritical domain (+ 4.4 at 827 °C with 2900 A/cm^{2[13]}). Moreover, the influence of electric current on ferrite-austenite phase transformation has not been studied.

In the above-mentioned context, the objective of this work is to study the influence of electric current on the C diffusion in iron with phase transformation in the inter-critical temperature domain. This study focuses on the influence of an electric current on ferrite (Fe- α)/ austenite (Fe- γ) phase transformation kinetics occurring in an ARMCO iron sample during a solid carburization experiment. Both experimental and modelling aspects of the electromigration of C in iron are explored. The experimental methodology is first described and solid carburization of an ARMCO iron during Joule heating in a Spark Plasma Sintering (SPS) apparatus is presented. Then a model accounting for the C diffusion, the iron phase change and the influence of the electric current on C diffusion is introduced. This model explains both the polarity effect on C diffusion and the



Fig. 2—Principle of carburization during SPS thermal treatment with phase transformation inside an ARMCO iron sample. The cross-section of an ARMCO iron ring is represented (vertical axis symmetry) and stretched for more clarity. C concentrations C_0 , C_1 and C_2 are linked to the Fe–C phase diagram (Fig. 3).

modification of ferrite to austenite phase change kinetics. A detailed sensitivity study is presented to discuss the influence of the different parameters of our model. Lastly, the results of the SPS thermal treatments simulations are compared with the experimental observations (optical microscopy, phase quantification, microhardness indentation) in the framework of the electromigration theory.

II. MATERIALS AND TECHNIQUES

A DC current Spark Plasma Sintering apparatus (HPD25 model from FCT System Company) is used to apply an electric current through a sample during a thermal treatment. The temperature of the sample increases due to Joule heating. The temperature level is controlled varying the current density. The current in the sample is pulsed: it is equal to I_{peak} during a part Δt of the period τ of the pulse. For all the experiments, a pulsed current with a ratio $\Delta t/\tau = 2/3$ and a frequency of 66.7 Hz. The electric current density is then equal to $j_{\text{peak}} = I_{\text{peak}}/S$, with S the sample cross section.

Figure 2 presents the principle of experimental setup and the phenomena induced by C diffusion inside the sample. The ARMCO iron sample is placed between the upper and the lower graphite punches. Two type K thermocouples, 1 mm in diameters are placed in holes 2.5 mm in depth, one near the interface (T_{C1}) and another one (T_{C2}) in the middle of the sample. From the ambient temperature, the sample is heated *via* the Joule effect to the target temperature in the intercritical domain. The electric current density is regulated so that the temperature T_{C1} follows the imposed thermal cycle. The temperature difference between T_{C1} and T_{C2} reaches a maximum of 15 °C at the beginning of the heating phase and then decreases and does not exceed 2 °C after 2 hours. Therefore, the temperature gradient between the interface and the middle of the sample is not significant. The SPS apparatus measures and stores the root-mean square value of the electric current intensity:

$$I_{\rm rms} = \sqrt{\frac{1}{\tau} \int_{0}^{\tau} (I(t))^2 \mathrm{d}t}$$
 [2]

During the holding stage $I_{\rm rms}$ varies between 2.3 and 2 kA. This variation is due to creep deformation which reduces the sample height during the experiment and due to the sample electrical resistivity variation. The punches cooling conditions are not controlled and thus, the electric current depends on the choice of the temperature level. Moreover, the cooling kinetics at the end of the experiment is not controlled but it is measured thanks to the thermocouples; the cooling stage lasts 4.5 minutes. To ensure a good electric contact, the lower value of the force between the two punches is set to 5 kN equivalent to a pressure of 7 MPa. Above 736 °C, iron is not anymore elastic and deforms continuously^[5] under the force applied between the punches. However, if the sample section is larger than 7 cm^2 , the deformation becomes lower than 10 pct at



Fig. 3—Schematic iron–carbon phase diagram. The boundary condition C_0 of the C concentration at the interface is determined by the equilibrium concentration between C graphite and Fe at a given temperature. The intercritical domain of temperature is filled in orange (Color figure online).

950 °C during 7 hours. Moreover, the heat source due to Joule effect induces temperature gradients in the sample. To minimize these temperature gradients, the sample has the shape of a hollow cylinder which inner diameter, d_i , outer diameters, d_o , and height, h, are equal to:

 $d_{\rm i} = 40 \, {\rm mm}, \, d_{\rm o} = 50 \, {\rm mm} \, {\rm and} \, h = 6 \, {\rm mm}.$

In order to decorrelate the influence of the electric current and the thermal diffusion, carburization experiments were also realized without Joule heating. A specific radiative heating furnace was used in which the sample is placed between two punches (top and bottom) which apply the same pressure than in the SPS apparatus. Due to the heating process, the sample is now a cylinder which is 1 cm in diameter and 1 cm in height but the top and bottom surfaces were prepared with the same procedure than for SPS experiments.

Our work aims to analyze the electromigration of C in iron related with phase transformation. Considering the Fe-C thermodynamic diagram (Figure 3), C might significantly diffuse in iron in the intercritical domain (temperature between 736 °C and 911 °C). So, three target temperatures were chosen: 775 °C, 825 °C and 875 °C. In the intercritical domain, C diffusion promotes ferrite to austenite transformation leading to an austenite/ferrite interface (Figure 2). Due to the drift velocity induced by electromigration, we expect different C diffusion depth from these two interfaces. The former literature results on electromigration of C in Fe combined with the prediction model described in Section IV allow to estimate that a 7 hours long isothermal treatment would lead to a significant diffusion depth and a significant difference between the diffusion depths between the anode and the cathode. Despite the thickness of the interface between ferrite and austenite is of the nanometer scale, it is represented as a thick interface on the Figure 2 in order to identify the characteristic values of the C concentrations. A microstructure gradient after cooling is expected due to the austenite transformation into ferrite and pearlite. Identifying the ferrite/austenite phase change front and the pearlite concentration profile will then give us information about C diffusion during the electro thermal treatment. This is the key point of this experimental methodology: a simple optical observation of the microstructure allows to extract information about the phase change front position and the C concentration in austenite. This analysis method is possible only because the phase change during the thermal treatment give rise to a significant microstructure change after cooling. It is much simpler than using C¹⁴ concentration profile as used in previous studies.^[12–16]

To ensure C diffusion from graphite to iron, the contacting surfaces have to be polished (SiC grinding paper with grade down to 4000, polycrystalline diamond suspensions with particles 6, 3 and 1 μ m in size). At the end of each experiment, the samples have been cut and the sections have been polished and chemically etched with NITAL solution (4 pct nitric acid solution in ethanol) during few seconds in order to reveal their microstructure. Optical images of the sample's microstructure are used to identify the phase change front position. Microhardness indentation and phase quantification are also used to evaluate the C distribution after experiment. Vickers hardness measurements were performed on a Buehler machine with a load of 0.2 kg and a step of 25 μ m between indentations in staggered rows to draw hardness profiles along the samples. The uncertainty on hardness measurements is 10 HV0.2. Image analysis of binarized experimental microstructures is used to quantify pearlite and ferrite phases fraction, f_p and f_f respectively ($f_p + f_f = 1$), function of the distance from the electrodes (Carbon/Iron interfaces). We assume here that measured volume fractions are equal to mass fractions f_p and f_f (the error associated to this assumption is less than 1 pct, far below the uncertainty of volume fraction measurements). We assume that at first order the carbon concentration in pearlite and in ferrite are equal to $C_p = 0.77$ wt pct and $C_f = 0.02$ wt pct respectively.^[17] The corresponding carbon concentration is then calculated as (Figure 3):

$$C_{\rm C} = f_{\rm p}C_{\rm p} + f_{\rm f}C_{\rm f}$$
^[3]

III. EXPERIMENTAL RESULTS

A. Thermal Treatments with Electric Current

Figure 4 shows the microstructure near the cathode and the anode interface respectively, obtained after the treatments. The NITAL chemical etching reveals the microstructure of the iron sample. As expected, three zones appear. Two of them are close to the interfaces made of pearlite and ferrite mixture corresponding to the former austenite before cooling down to ambient temperature. The pearlite content decreases when the distance from the interface increase since the C concentration decreases. As ARMCO iron is almost pure (99.98 pct), and as the cooling rates are slow, no residual austenite or martensite is observed. The third zone is the



Fig. 4—Image of the sample's microstructures perpendicular to the C diffusion direction after a thermal treatment in SPS at 775 $^{\circ}$ C, 825 $^{\circ}$ C and 875 $^{\circ}$ C for 7 h. For each temperature, the electric current density is given in Table I.

central zone: it is made of large ferrite grains that have not been transformed in austenite during the thermal treatment because the C concentration remained low enough. As can be seen on the Figure 4, the interface between these zones are really sharp. Then it is possible to identify the positions of the former austenite—ferrite transformation fronts before cooling.

Table I gathers the measurements of phase change front positions resulting from the SPS experiments. The thickness of the sample affected by the carbon diffusion is larger for higher temperature: the mean value of the front's displacement, d, equal to $(233 \pm 10) \mu m$ at 775 °C and increases up to $(955 \pm 10) \mu m$ at 875 °C. The displacements of the phase change fronts measured from the anode and from the cathode are different for all experimental temperatures. Indeed, the difference between the fronts' displacements, σ_d , increases with the temperature, soaring from $(45 \pm 10) \mu m$ at 775 °C to $(450 \pm 10) \mu m$ at 875 °C. The main conclusions from the experimental observations are the following:

- Our experiments showed that the ferrite to austenite phase transformation kinetic is faster in the direction of the electric current (from the anode to the cathode) and hindered in the opposite direction. This is expected with the electromigration phenomenon since the drift velocity is in the same direction as the electric current if $Z^* > 0$.
- The difference of front displacements from anode and cathode also increases when the temperature increases. This is also expected since this difference is mainly due to the drift velocity which is proportional to the diffusion coefficient (Eq. [13] demonstrated in Section IV). The positions of these fronts on the an-

ode and the cathode sides reveals the influence of the electric current on the C diffusion during the heat treatment with Joule effect.

The Mean Values of the Front Displacements Increase with Higher Temperature as Expected Since Diffusion is a Thermally Activated Phenomenon.

B. Thermal Treatment Without Electric Current

Figure 5 shows the sample's microstructure after the same thermal treatments (temperature, duration) than in the SPS. Three more treatments were realized at 875 °C for duration ranging from 1 to 5 hours. The thickness of the zone which has been transformed in austenite during the thermal treatment can also be easily identified and measured (Table I). In these conditions (radiative heating without electric current), the thickness should be the same on both sides of each samples. This is not the case, which means that the quality of the interface between graphite and iron is not reproductible.

However, despite the variability of the interface, comparing results for thermal treatment with no electric current and the one with current, two conclusions arise:

- The mean value of the phase change fronts displacements, d, is significantly lower compared to the one obtained when the sample has been heated by Joule effect in the SPS. We may then expect that the electric current influence the diffusion coefficient of C in iron. This assumption will be confirmed in Section IV thanks to simulations.
- Without electric current, σ_d (bottom front position minus top front position) is either negative or posi-



Fig. 5—Image of the sample's microstructures perpendicular to the C diffusion direction after a thermal treatment in a radiative furnace at 775 °C, 825 °C and 875 °C for 7 h.

tive. So there is a clear influence of the electric current on σ_d at 875 °C ($\sigma_d = 450 \ \mu m$ in SPS $v_s - 110 \ \mu m$ in the radiative furnace). At lower temperatures (775°C and 825 °C), the order of magnitude of the absolute value of σ_d is the same with and without electric current, but σ_d is systematically positive with electric current which confirm the directional influence of the electric current on the C diffusion. As the directional effect of the electric current is due to the equivalent charge of C in iron (Eq. [1]), it is thus clear that its determination will suffer of larger uncertainties at low temperature than at high temperature due to the varying quality of the graphite/iron interface from one sample to another (despite following identical surface preparation).

To interpret these experimental observations, a model accounting for the allotropic phase change and the electromigration of C in iron is presented here after. The objective is to predict the microstructure evolution during the carburization of iron assisted by electric current by fitting diffusion and electromigration parameters in this model.

IV. MODEL OF C DIFFUSION IN IRON WITH ELECTROMIGRATION

A recently developed model was proposed by Mathevon *et al.* to predict austenite-ferrite transformation kinetics in steels.^[18] It is built on the prediction of diffusion and concentration profiles for all elements in iron in the whole domain, including the phase transformation interface volume. The ferrite/austenite interface

is displaced to minimize the Gibbs energy of the system calculated thanks to thermodynamic data extracted from Thermocalc TCFE6 database. This model has been modified in order to account for the influence of the electric current on the C diffusion.

In most existing theories of the electric current-induced mass transfer, the driving force for electromigration comprises two components, one is the direct force F_d from the external current stress causing the columbic force, and the other is the "electron wind" force F_w from the momentum transfer of electrons colliding with ions. The associate models originate from Fiks^[10] and Huntington and Grone^[11] first mathematical formulations who treated the electron wind force with a ballistic approach (collisions between mobile points defects and charge carriers). Assuming a 1D geometry along x direction, Eq. [4] gives the equivalent force exerted on an atom:

$$F_{\rm d} + F_{\rm w} = eZ^*E \tag{4}$$

with

$$E(x,t) = -\frac{\partial \phi(x,t)}{\partial x} = \rho(x)j(t)$$
 [5]

e is the Coulomb charge, *E* the electrical field, ϕ the electrostatic potential, *j* the current density and ρ the electrical resistivity. Z^* is the atomic equivalent effective charge of the atoms submitted to the electric current density. It sets the scale of the driving force as the balance between the direct electrostatic force and the electron force. It is one of the most important quantity to evaluate the magnitude of electromigration.

Tomore (OC)		S	Auster	lite 15			575		
I chipperature (C)		0	70	0.1			610		
Electric Current Density jneak (A/cm ²)	381	0	358	0	397	0			
Duration (h)	7	7	7	7	7	1	3	5	7
Cathode/Top Front Displacement (μm)	210	25	410	327	730	262	425	460	725
Anode/Bottom Front Displacement (µm)	255	165	520	137	1180	352	605	580	505
$\langle q \rangle$ (mm)	233	95	468	232	955	307	515	520	615
σ_{d} (µm) (Anode-Cathode) or (Bottom-Top)	45	70	105	- 95	450	45	06	60	-110
$K = D_{\gamma}/D_{Agren}$	1.00 ± 0.04	0.17 ± 0.13	0.69 ± 0.02	0.18 ± 0.07	0.73 ± 0.01	0.43 ± 0.06	0.42 ± 0.07	0.39 ± 0.05	0.31 ± 0.06
Z^*_{γ}	17 ± 4		25 ± 2		39 ± 1				

The continuity equation associated with the Fick's law gives the diffusion equation in 1D controlling the distribution of $C^{[19]}$:

$$\frac{\partial C(x,t)}{\partial t} = \frac{\partial}{\partial x} \left(C(x,t) \frac{D(x)}{RT} \frac{\partial \mu(x)}{\partial x} \right)$$
[6]

where *C* is the concentration of carbon, *T* is the temperature, *D* is the diffusion coefficient of carbon, *R* is the ideal gas constant, μ is the electrochemical potential of carbon. Assuming an ideal dilute solution of carbon in iron, at a given temperature, the electrochemical potential of C in a dilute solution submitted to an electric field can be written as^[20] (in molar unit)

$$\mu(x) = \mu^{0}(x) + RT \ln C(x) + FZ^{*}(x)\Phi(x,t)$$
 [7]

$$\frac{\partial \mu(x)}{\partial x} = \frac{\partial \mu^0(x)}{\partial x} + RT \frac{1}{C(x,t)} \frac{\partial C(x,t)}{\partial x} + F \frac{\partial (Z^*(x)\phi(x,t))}{\partial x}$$
[8]

where F is the Faraday constant, defined as the product of the Coulomb charge e and the Avogadro constant N_A :

$$F = eN_{\rm A}$$
[9]

Equations [6] and [8] lead to the diffusion equation of C:

$$\frac{\partial C(x,t)}{\partial t} = \frac{\partial}{\partial x} \left(D(x) \frac{\partial C(x,t)}{\partial x} \right) + \frac{\partial}{\partial x} \left(\frac{C(x)D(x,t)}{RT} \frac{\partial \mu^0}{\partial x} \right) \\ + \frac{\partial}{\partial x} \left(\frac{C(x,t)D(x)F}{RT} \frac{\partial (Z^*(x)\Phi(x,t))}{\partial x} \right)$$
[10]

Thanks to the second term of the right-hand side, this equation can be used in the whole volume of the system (volume between the two electrodes on Figure 2) and remains valid in austenite and ferrite phases and in the interface region of width δ between these two phases. The experimental results show that the austenite/ferrite interface is quite sharp. Moreover, we do not have any experimental evidence of the real interface thickness. Thus, the interface thickness δ is set to 10 μ m. This value is not especially related to the experimental uncertainties of the position of the interface. This value is a compromise between the numerical accuracy and the computational time. We indeed checked that the results do not depend on the interface thickness δ . In austenite and in ferrite, the chemical potential μ^0 is constant, so its derivative is equal to 0. However, in the interface, we assume that μ^0 varies linearly between its value in austenite on one side and in ferrite on the other side (μ_{α}^{0} and μ_{ν}^{0} respectively). The numerous defects at the interface between ferrite and austenite, enhance the C diffusion in this region. Thus we choose to set the C diffusion coefficient in the interface equal to the one in ferrite, which is always faster than the diffusion in austenite.^[18] The effective charge of C in iron is constant

Table II. Values of the C Concentration on the Phase Change Interface in Ferrite (C_2) and in Austenite (C_1) and Between Austenite and Graphite (C_0)

Temperature (°C)	775	825	875
$ \frac{C_0 \text{ (Wt Pct)}}{C_1 \text{ (Wt Pct)}} \\ C_2 \text{ (Wt Pct)} $	0.79 0.46 0.0143	0.93 0.241 0.0095	1.09 0.084 0.0043

Values calculated with Thermocalc TCFE6 database for the iron/graphite system.

with different values, Z_{γ}^* in austenite and Z_{α}^* in ferrite. In the interface, the effective charge is simply given by the average

$$Z^*_{\alpha+\gamma} = \frac{Z^*_{\gamma} + Z^*_{\alpha}}{2}$$
[11]

With the above assumptions and assuming constant properties on each phase, Eq. [10] combined with Eq. [5] gives rise to Eq. [12], in which the drift velocity due to the electric field v_d which has already been introduce by^[21] appear (Eq. [13]). v_d is a convenient parameter to interpret the experimental results.

$$\frac{\partial C(x,t)}{\partial t} - \frac{\partial \mu^0}{\partial x} \frac{D}{RT} \frac{\partial C(xt)}{\partial x} + v_{\rm d} \frac{\partial C(x,t)}{\partial x} = D \frac{\partial^2 C(x,t)}{\partial x^2}$$
[12]

with

$$v_{\rm d} = \frac{DZ^*}{RT} FE$$
 [13]

The diffusion equation (Eq. [10]) is solved using 1D implicit Finite Difference scheme. The choice of the numerical scheme and the final discretized equation are given in the appendix. The advantage of this approach lies in the fact that a single equation is used to solve the C diffusion in the whole domain of interest, including the austenite, the ferrite and the interface regions. In our experiments, as iron is carburized in the intercritical domain (the temperature *T* is lower than 911 °C and higher than 736 °C) then, C first diffuses in α -iron; when the C has saturated α -iron then it transforms into γ -iron.

The phase change and interface migration are based on Gibbs Energy Minimization.^[18] At each time step, the carbon concentration profile is calculated for three configurations:

- 1. the interface does not move;
- 2. the interface moves one step forward and
- 3. the interface moves one step backward.

From the concentration profile of each configurations, the Gibbs energy is calculated and the configuration which exhibits the lowest Gibbs energy is used for the next time step.

A. Simulation Set-Up

The numerical solution of the model has been implemented for two ferrite/austenite interfaces to simulate iron carburization as experimented in SPS and represented in Figure 2. A rectangular cross-section sample is represented initially as ferrite with a small fraction of austenite at both ends; two ferrite/austenite interfaces are placed between the two phases. The electric current is directed along increasing abscissa x. The anode corresponds to the position x = 0 and the cathode is at the position x = L. The austenite fraction grows as the C diffuses through existing austenite, reaches the α/γ interface and enriches the ferrite near this interface.

All the results are detailed for the simulations of the Joule effect treatments as described before. The simulation parameters are:

- the sample is 4 mm long with a rectangular cross-section, S, of 7 cm².
- the electric current density through the sample is given in Table I.
- the thickness of the ferrite/austenite interfaces is equal to $\delta = 10 \ \mu m$.
- the effective charges of C in iron are Z_{α}^{*} in ferrite and Z_{γ}^{*} in austenite. A first guess for these values is taken from Figure 1(a) depending on the temperature level in ferrite and current density in austenite.
- The carbon concentration at the boundary nodes (the boundary with electrodes on Figure 2) is set equal to the maximum value of carbon concentration in austenite (C_0 on Figure 3, values in Table II).
- The diffusion coefficients depend on the temperature and the carbon concentration. They are calculated at each node from equations proposed by Ågren in ferrite^[22] and austenite^[23] (Eqs. [14] and [15]).

$$D_{\alpha} = 0.02 \frac{m^2}{s} \times \exp\left[-\frac{10115K}{T}\right] \exp\left\{0.5898 \left[1 + \frac{2}{\pi} \arctan\left(1.4985 - \frac{15309K}{T}\right)\right]\right\}$$
[14]

$$D_{\gamma} = 4.53 \frac{m^2}{s} \times 10^{-7} \left[1 + y_{\rm C} (1 - y_{\rm C}) \frac{8339.9K}{T} \right] \\ \times \exp\left\{ - \left(\frac{1K}{T} - 2.221 \times 10^{-4} \right) (17767 - 26436y_{\rm C}) \right\}$$
[15]

with $y_{\rm C} = \frac{x_{\rm C}}{1-x_{\rm C}}$, $x_{\rm C}$ being the mole fraction of C and T the temperature in K.

 The electrical resistivity also depends on the C concentration. Its value is calculated using Eq. [16]^[24]:

Table III. Sensitivity Coefficients on Diffusion and Electromigration Parameters

<i>T</i> (° C)	775	825	875	$T(^{\circ} C)$	775	825	875	
Sensitivity Coefficients of d (Output)				Sensitivity Coefficients of σ_d (Output)				
$\frac{\partial \left(\frac{\Delta d}{d}\right)}{\partial \left(\frac{\Delta D_{\mathcal{X}}}{D_{\mathcal{X}}}\right)}$	1.4×10^{-4}	9.5×10^{-3}	8.6×10^{-4}	$\frac{\partial \left(\frac{\Delta \sigma_d}{\sigma_d}\right)}{\partial \left(\frac{\Delta D_{\chi}}{D_{\chi}}\right)}$	- 1.4	-7.0×10^{-1}	-4.0×10^{-1}	
$\frac{\partial \left(\frac{\Delta d}{d}\right)}{\partial \left(\frac{\Delta D_{\gamma}}{D_{\gamma}}\right)}$	5.0×10^{-1}	5.0×10^{-1}	5.0×10^{-1}	$\frac{\partial \left(\frac{\Delta \sigma_d}{\sigma_d}\right)}{\partial \left(\frac{\Delta D_{\gamma}}{D_{\gamma}}\right)}$	2.6	1.6	1.4	
$\frac{\partial \left(\frac{\Delta d}{d}\right)}{\partial \left(\frac{\Delta Z_{\chi}^{*}}{Z_{\chi}^{*}}\right)}$	-2.9×10^{-4}	6.5×10^{-4}	1.6×10^{-3}	$\frac{\partial \left(\frac{\Delta \sigma_d}{\sigma_d}\right)}{\partial \left(\frac{\Delta Z_{\alpha}^*}{Z_{\alpha}^*}\right)}$	- 1.4	-6.0×10^{-1}	-4.0×10^{-1}	
$\frac{\partial \left(\frac{\Delta d}{d}\right)}{\partial \left(\frac{\Delta Z^*_{\gamma}}{Z^*_{\gamma}}\right)}$	2.4×10^{-3}	2.8×10^{-3}	4.0×10^{-3}	$\frac{\partial \left(\frac{\Delta \sigma_d}{\sigma_d}\right)}{\partial \left(\frac{\Delta Z_{\gamma}^*}{Z_{\gamma}^*}\right)}$	2.7	1.6	1.4	

$$\rho(T,C) = \alpha + b_1 T + b_2 T^2 + b_3 C^{\frac{1}{4}}$$
[16]

with the C concentration C in weight percent, the temperature T in °C, $\alpha = 6.51 \times 10^{-8} \Omega \text{ m}$, $b_1 = 4.74 \times 10^{-10} \Omega \text{ m} \circ \text{C}^{-1}$, $b_2 = 8.89 \times 10^{-13} \Omega \text{ m} \circ \text{C}^{-2}$ and $b_3 = 1.22 \times 10^{-7} \Omega \text{ m} (\text{wt pct})^{-1/4}$.

B. Model Parameters Sensitivity Study

The influence of our model parameters (the effective charges and the diffusion coefficients of C in iron phases) is examined in a multi-parameter study. Table III gathers the results of the "One-At-a-Time" sensitivity study on the influence of these parameters on the phase change kinetics obtained for 7 hours carburization simulated at 775 °C, 825 °C and 875 °C. Simulations were first done with initial input parameters as described in Section IV-A and the resulting mean displacement d and difference of displacement σ_d of the two α/γ interfaces are recorded as nominal output values. When one input parameter is modified, the output values change consequently. The impact of the model parameters on the carburization kinetics simulated are expressed by the sensitivity coefficients. They are calculated as follows:

$$\frac{\partial \left(\frac{\text{Aout}}{\text{out}}\right)}{\partial \left(\frac{\text{Ain}}{\text{in}}\right)}$$
[17]

where Δ out is the variation of the output value (mean d or difference of displacement σ_d) stemmed from Δ in the variation of the input parameter (for example the diffusivity of C in ferrite D_{α}), when out and in are the nominal values of the output and input parameters respectively.

The sensitivity study is used to set up a methodological approach to identify the most important parameters. The first conclusion from the sensitivity coefficients in Table III is that only the diffusion coefficient in austenite D_{γ} has a significant influence on the mean displacement of the interfaces *d*. Diffusion kinetics on both anode and cathode sides are faster with a higher D_{γ} allowing C to reach quickly the interfaces. The diffusion of C in austenite is critical for the carburization kinetics because C atoms have to diffuse through austenite to reach the interface and then to enrich ferrite.

Secondly, it appears that all model parameters have a significant influence on the difference of displacement $\sigma_{\rm d}$ between anode and cathode interfaces. The sensitivity coefficients for the diffusion coefficient in ferrite D_{α} and the effective charge of C in ferrite Z^*_{α} are negative; they are positive for the diffusion coefficient in austenite D_{γ} and the effective charge of C in austenite Z_{γ}^* . The drift velocity of carbon v_d is proportional to the product of D, Z^* and ρ (Eq. [13]). On one hand, higher parameters in ferrite lead to a smaller σ_d due to a greater drift velocity of carbon in ferrite v_d^{α} . It allows more C to migrate from the anode to the cathode sides and emphasizes the phase transformation kinetic on the cathode. On the other hand, higher parameters in austenite lead to a wider σ_d . In this case, both the diffusion and the electromigration of C in austenite are enhanced (through v_d^{γ}). Thus, C atoms reach quickly the α/γ interface on the anode side and the phase transformation is enhanced. Our model and its sensitivity study reveal that the drift velocity leads the C diffusion and the carburization kinetics during a heat treatment assisted by electric current.

From this sensitivity study, we define a methodology to fit the model parameters:

- the diffusion coefficient of C in austenite D_{γ} is the first to be adjusted in order to well represent the mean value of α/γ interfaces displacement, d. This first step implicitly assumes that the electric field may influence the diffusion coefficient of C in iron despite no physical



Fig. 6—Comparison of simulation predicted kinetics (curves) and experimental SPS results (points) after 7 h, from the anode and from the cathode. Experimental measurements are displayed with the same color code for the temperature. Only one point of the experimental kinetics is displayed at the end of the thermal treatment (7 h): plain triangles pointing either up or down are for the final phase change front positions at the anode and at the cathode respectively. The circles show the experimental mean positions of the phase change fronts (Color figure online).

phenomena to explain this influence have been identified. As the C diffusion in Fe depends on the C concentration (Eq. [15]), the diffusion coefficient proposed by Agreen^[23] is then multiplied by a factor K.

- Then, from the interface displacement difference, σ_d , three parameters remain to be identified: Z_{α}^* , Z_{γ}^* and D_{α} . Considering the Figure 1(b), Z_a^* slightly depends on the temperature level and on the current density, it is then considered constant and equal to + 3.5. As the influence of D_a^* is lower than the one of Z_{γ}^* , then we assume that the diffusion coefficient in ferrite is not influenced by the electric current. Thus, the interface displacement difference, σ_d , allows identifying the equivalent charge of C in austenite Z_{γ}^* .

The experimental methodology and the model lead us to assume that the electric field may have an influence on the diffusion coefficient of C in austenite. This is a new assumption that have never been considered in previous studies in which only the equivalent charge of C in iron has been identified.^[12–16] However D_{γ} and Z_{γ}^* are the two parameters that have the largest influence on the measured quantities (*d* and σ_d), then we may at least have a first trend of the influence on the electric current on these parameters.

C. Simulation Results

The model has first been used to simulate the C diffusion and phase change in the sample treated in the radiative furnace, *i.e.* without electric current. As a result, the mean value of the phase change front displacements d were overestimated. As d mainly



Fig. 7—Carbon profiles from simulation of 1-, 3- and 7-h carburization at 825 °C. In red: thermal diffusion alone; In black: thermal diffusion and electromigration are accounted for. The red dashed lines show the final experimental austenite/ferrite interface positions (Color figure online).

depends on the C diffusion coefficient in austenite, the diffusion coefficient in austenite had then been multiplied by a factor K (Table I) to get the same value of d than experimentally. As a conclusion, when there is no electric current, accounting for the variability of the quality of the graphite/iron interface, the diffusion coefficient in austenite is significantly lower than the one proposed by Agreen.^[23] The initial composition and microstructure of the ARMCO iron, might explain the difference. Thermal treatments were realized during different durations (1, 3, 5 and 7 hours) at 875 °C. As can been seen in Table I, the diffusion coefficient of C in austenite slightly decreases when the duration of the thermal treatment increases. This might be explained by the fact that the interface quality between graphite and iron changes during the thermal treatment.

Then, thanks to the results of the sensitivity study, D_{γ} and Z_{γ}^* have been determined (Table I) for the treatment in the SPS, *i.e.* with electric current:

- D_{γ} is first fitted setting $Z_a^* = Z_{\gamma}^* = 0$. The dashed line (Figure 6) represents the kinetic of the phase change front in this condition and the final position correspond to the experimental value of *d*. The phase change front position is determined from the C concentration profile. These profiles have been plotted on Figure 7 (black lines) for T = 825 °C at different time. The positions of the ferrite/austenite phase transformation interfaces correspond to the C concentration gaps, dropping from around 0.25 to 0.01 wt pct C in austenite and ferrite respectively.
- With the fitted value of D_{γ} , Z_a^* is set to 3.5 and Z_{γ}^* is then determined to find the same value of σ_d than experimentally. The position of the austenite/ferrite interface is determined by the same way than for the first stage of the fitting procedure. However, as the C



Fig. 8—Comparison of C profiles after 7 h carburization at 825 $^{\circ}$ C from simulation, microhardness measurements and phase quantification.

atom has a positive charge, the kinetic of the austenite/ferrite near the anode is faster than the one near the cathode (Figure 7, red curves). The plain curves on Figure 6 represent the simulated interfaces positions kinetics and compare the final positions with the experimental values.

Figure 7 also shows an interesting feature of the C diffusion. As C diffuses into Iron, C enrichment becomes high enough to allow ferrite to austenite transformation even if all the ferrite has not been saturated (curve for t = 1 hours). This is due to the assumption that the C concentration at the interface with graphite is equal to the maximum value of C concentration in austenite (C_0).

To check this assumption, the final simulated C concentration profile is compared to the experimental one. Results for T = 825 °C are shown on Figure 8. Image analysis of experimental microstructures was used to quantify pearlite and ferrite phases distribution and calculate the corresponding carbon content. Electron Probe MicroAnalysis (EPMA) was also carried out to obtain the carbon content in C-rich areas (first 300 μ m on both sides). Vickers micro-hardness measurements were also performed (weight = 0.2 kg, step = 25 μ m). The experimental positions of the ferrite/austenite phase transformation interfaces are easily identified by the C concentration gap dropping between 0.25 and 0.01 wt pct C corresponding to the values of C_1 and C_2 of Table II at 825 °C. The austenite ferrite interface can also be identified but with a lower accuracy looking at the micro-hardness gap dropping from around (150 \pm 10) to (90 \pm 10) HV0.2. These observations are coherent with the microstructures observed on Figure 4. The agreement between the image analysis technic and EPMA is excellent far enough from the anode and cathode where ferrite and pearlite are both present. Near the electrodes, the pearlite fraction is so high that image analysis is less accurate and underestimates the C concentration. EPMA is the most accurate technique

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for high C concentration. The simulation results give the same trend than the experimental one, but slightly overestimate the C concentration. This might be due to the choice of the boundary condition. Using the experimental value of the C boundary concentration leads to an increase of the diffusion coefficient between 5 and 10 pct depending on the temperature level. However, this does not change the difference observed between the diffusion coefficient with and without electric current.

V. DISCUSSION AND CONCLUSIONS

An original experimental methodology to study the electromigration of C in iron with phase change is proposed. ARMCO iron samples were submitted to solid carburization during a thermal treatment using Joule heating. As C diffuses and enriches the sample during the heat treatment, initial ferrite transforms into austenite. The carburization of iron in the intercritical domain allows an easy observation of the interface of ferrite/austenite phase transformation and the microstructure after cooling. The C diffusion is enhanced in the direction of the electric current and hindered in the opposite direction, due to the electromigration phenomenon. The influence of the electric current on the C diffusion leads to different positions of the ferrite/austenite interface from the anode and from the cathode; this asymmetry increases with the temperature level.

C diffusion and iron phase transformation model has been developed accounting for the electromigration phenomenon. It is used to predict the kinetics of ferrite/austenite interface displacement and the C distribution resulting from the carburization of the ARMCO iron, with or without electric current. From the sensitivity study it has been chosen to fit two parameters: the diffusion coefficient and the equivalent charge of C in austenite D_{γ} , and Z_{γ}^* . In this configuration, carburization with phase change, these two parameters can be identified separately. In previous studies^[12–16] of C electromigration in a single solid phase, D_{γ} have been considered constant and Z_{γ}^* is identified from the C concentration profile: the two parameters cannot be identified separately since their influence is correlated through the drift velocity.

As seen on Figure 1(b), the values of Z_{γ}^* previously reported in the literature are scattered and fluctuate from + 7 to + 15 for a similar current density (around 370 A/cm²). Our results for Z_{γ}^* are higher than these values: Z_{γ}^* increases from (+ 17 ± 4) at 775 °C to (+ 39 ± 1) at 875 °C. Actually, the data available in the literature concerns fully austenite specimens and the influence of the electric current on the C diffusion coefficient in austenite has not been considered. Moreover our study concerns iron transforming from ferrite to austenite. The effective charge of C is indeed "effective" as it is a physical parameter to represent the apparent behavior of C submitted to an external electrical force while iron experiences phase change. The electric current significantly increases the C diffusion coefficient in austenite. The influence of the electric current is more important at low temperature (Table I): the carbon diffusion coefficient in austenite has been multiplied by almost 6 at 775°C, 4 at 825 °C and 2 at 875 °C which is much beyond the uncertainties due to the experimental conditions (mainly the quality of the graphite/iron interface) and the assumptions for the model.

This study clearly shows that two phenomena occur in an iron-carbon alloy during a thermal treatment with Joule heating: electromigration and enhancement of diffusion. Electromigration has already been characterized either in ferrite or in austenite.^[12-16] In these conditions it has been assumed that electric current does not influence C diffusion. In our conditions, carburization of iron inducing phase change, the two effects can be evaluated despite the experimental uncertainties and model assumptions. However, an independent evaluation of these two effects would be quite interesting. This might be done using alternative electric current instead of pulsed direct current or direct continuous currents. Indeed, with alternative direct current, only the influence of the electric current on the diffusion coefficient would remain, since the directional electromigration phenomenon would be neutralized. Also, the use of iron alloy with a lower value of Ae1 would allow to study C electromigration in austenite without the phase change. This will give rise to further studies.

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CONFLICT OF INTEREST

On behalf of all authors, the corresponding author states that there is no conflict of interest.

APPENDIX: DISCRETIZATION OF THE DIFFERENTIAL DIFFUSION EQUATION ACCOUNTING FOR THE PHASE CHANGE AND ELECTROSTATIC EFFECT

The equation to be solved is Eq. [10] which is recalled below, rename A1 here

$$\frac{\partial C(x,t)}{\partial t} = \frac{\partial}{\partial x} \left(D(x) \frac{\partial C(x,t)}{\partial x} \right) + \frac{\partial}{\partial x} \left(\frac{C(x,t)D(x)}{RT} \frac{\partial \mu^0}{\partial x} \right) \\ + \frac{\partial}{\partial x} \left(\frac{C(x,t)D(x)F}{RT} \frac{\partial (Z^*(x)\Phi(x,t))}{\partial x} \right)$$
[A1]

Equation [A1] is discretized considering the discretization scheme below at each node *i*:

For the left-hand side of Eq. [A1] a first order time discretization scheme is used:

$$\left(\frac{\partial C}{\partial t}\right)_{i} = \frac{C_{i}^{t+\Delta t} - C_{i}^{t}}{\Delta t}$$
 [A2]

In the first term of the right hand-side of Eq. [A1]:

$$\left(\frac{\partial}{\partial x}\left(D\frac{\partial C}{\partial x}\right)\right)_{i} = \frac{\left(D\frac{\partial C}{\partial x}\right)_{i+1/2} - \left(D\frac{\partial C}{\partial x}\right)_{i-1/2}}{\Delta x}$$
[A3]

$$\left(D\frac{\partial C}{\partial x}\right)_{i+1/2} = D_i \frac{\partial C}{\partial x}\Big|_{i+\frac{1}{2}} = D_i \frac{C_{i+1} - C_i}{\Delta x} \qquad [A4]$$

$$\left(D\frac{\partial C}{\partial x}\right)_{i-1/2} = D_i \frac{\partial C}{\partial x}\Big|_{i-\frac{1}{2}} = D_i \frac{C_i - C_{i-1}}{\Delta x} \qquad [A5]$$

In this term, the concentrations are evaluated at time $t + \Delta t$ (implicit scheme) while the diffusion coefficient is calculated explicitly (at time t).

The discretization of the second term of the right-hand side in Eq. [A1]:

$$\left(\frac{\partial}{\partial x} \left(\frac{CD}{RT} \frac{\partial \mu^0}{\partial x}\right)\right)_i = \frac{\left(CD \frac{\partial \mu^0}{\partial x}\right)_{i+1/2} - \left(CD \frac{\partial \mu^0}{\partial x}\right)_{i-1/2}}{RT\Delta x} \quad [A6]$$

with

$$\frac{\left.\frac{\partial\mu^{0}}{\partial x}\right|_{i+\frac{1}{2}} = \frac{\mu^{0}_{i+1} - \mu^{0}_{i}}{\Delta x} \quad \frac{\partial\mu^{0}}{\partial x}\Big|_{i-\frac{1}{2}} = \frac{\mu^{0}_{i} - \mu^{0}_{i-1}}{\Delta x}$$
[A7]

and

$$CD|_{i+\frac{1}{2}} = \frac{C_i D_i + C_{i+1} D_{i+1}}{2} \quad CD|_{i-\frac{1}{2}} = \frac{C_i D_i + C_{i-1} D_{i-1}}{2}$$
[A8]

In Eqs. [A11] and [A12], the concentrations C are evaluated at time $t + \Delta t$ (implicit scheme) and all the other parameters are evaluated at time t.

And for the last term of Eq. [A1]:

$$\left(\frac{\partial}{\partial x}\left(\frac{CDF}{RT}\frac{\partial(Z^*\Phi)}{\partial x}\right)\right)_i = F\frac{\left(CD\frac{\partial(Z^*\Phi)}{\partial x}\right)_{i+1/2} - \left(CD\frac{\partial(Z^*\Phi)}{\partial x}\right)_{i-1/2}}{RT\Delta x}$$
[A9]

with

$$F\frac{\partial(Z^*\phi)}{\partial x}\Big|_{i+\frac{1}{2}} = F\frac{Z_{i+1}^*\phi_{i+1} - Z_i^*\phi_i}{\Delta x}F\frac{\partial(Z^*\phi)}{\partial x}\Big|_{i-\frac{1}{2}}$$
$$= F\frac{Z_i^*\phi_i - Z_{i-1}^*\phi_{i-1}}{\Delta x} \qquad [A10]$$

The products CD are calculated with Eq. [A8].

Equations [A1] through [A10] are discretized equations, which are implicit for the concentration. They lead to a tridiagonal matrix system solved using Thomas's Algorithm^[25] which is quite efficient from a computational point of view. As for every discretization scheme, the time step and space step are chosen small enough such that the results do not depend on their specific values. The space step is fixed and equal to 1 μ m during the whole simulation. The time scale has to be varied during the simulation from small increment (μ s) during the initial stages of the simulation to much larger one (100 s) at the end of the simulation. The value of the time step actually depends on the phase change front kinetic.

Two issues have to be discussed for the evaluation of the electrostatic potential at each node *i* and each time *t*:

- The first one is related to the time step. The electrostatic potential is link to the instantaneous electric current density. As explained in Section III, the electric current is pulsed at a frequency of 667 Hz. Considering this frequency, the use of the instantaneous value of the electric current density to describe electromigration would lead to huge computational duration. So, we assume that a continuous current density given rise to the same Joule effect (same electron matter interactions) than the pulse current density has the same influence on electromigration. This continuous current is actually the rms value of the instantaneous current. We checked a posteriori that the results are the same (not significantly different, considering numerical resolution) using the instantaneous value of the electric current and it rms value.

Equation [5] is then rewritten as

$$-\frac{\partial\phi(x)}{\partial x} = \rho(x)j_{\rm rms}$$
[A11]

- The calculation of ϕ_i is done integrating equation [A11] with the following discretization scheme:

$$\phi_{i+1} = \phi_i - \frac{\rho_{i+1} + \rho_i}{2} \Delta x j_{\text{rms}} \qquad [A12]$$

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