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Tailoring the mechanical properties of steel sheets using FeC films and diffusion annealing

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ABSTRACT

In this work amorphous FeC films were deposited on thin sheets of interstitial free steel using physical vapor deposition. Annealing treatments were then carried out to diffuse C from the coating into the substrate at temperatures lower than those traditionally used in carburizing treatments. The yield stress was shown to significantly increase with annealing temperature from ~120 MPa at 25 °C up to a maximum of 300 MPa at 630 °C without any significant loss of ductility. At 710 °C, a decrease in yield strength was related to the coarsening of carbides inside the IF steel (confirmed by atom probe tomography), and the associated reduction in the matrix solid solution carbon concentration (confirmed by thermoelectric power measurements). The through-thickness carbon diffusion profile was predicted using Fick's law and validated by Knoop hardness measurements. Yield strength predictions were accurate if the crystallization of the FeC film was taken into account as it controls the amount of carbon available to be diffused in the interstitial free steel substrate.

1. Introduction

Traditional techniques used to strengthen steel by carbon additions involve case hardening and bake-hardening. Case hardening is related to the diffusion of carbon in bulk materials to increase their surface hardness and strength and it includes many techniques such as: pack carburizing, gas or liquid carburizing and vacuum carburizing. All these processes require temperatures higher than 870 °C and hours of processing times [1–3]. These processes are generally used to case-harden the surface of thick materials and cannot easily be applied to harden thin sheets of steel [1]. The traditional process used to strengthen thin sheets of ultra-low carbon steels is bake-hardening. This heat treatment (170 °C for 20 min) is performed after the forming step in order to segregate free carbon to the dislocations. However, the increase of yield stress caused by this heat treatment is limited to +50–60 MPa because the amount of carbon initially present in solution in the steel has to be kept low enough to avoid room temperature ageing which would cause Lüder's instabilities to appear during forming [2]. Steel companies are interested in developing new methods which can further increase the yield stress of thin sheets, without compromising the ductility or processing capability. The new approach proposed here is to use an iron–carbon film deposited on the surface of a steel sheet by Physical Vapor Deposition (PVD). These films, which can be crystalline or amorphous, have a very high carbon content and therefore can act as carbon reservoirs during subsequent diffusion annealing [4,5]. The advantage of the iron–carbon system is that the adhesion with the IF substrate is excellent and the corrosion resistance is improved. PVD is already implemented in the steel industry [6] and can be used as a continuous processing technique to coat steel strips wider than 1.5 m [4]. The present scope is to diffuse carbon at temperatures lower than 800 °C with a more time efficient process than the traditional carburizing procedures. Depending on the annealing temperature and time the final sheet can have a gradient of carbon or a uniform distribution of carbon through thickness. Preliminary work on this technique was made by Scott et al. [4], where it was shown that these films can be used to

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strengthen a sheet of interstitial free steel. In the present work a detailed investigation of the influence of film thickness, annealing temperature, and annealing atmosphere on the diffusion process and on the related mechanical properties is presented.

2. Experimental procedure

2.1. Material and physical vapor deposition

The substrate material is a fully recrystallized 0.197–0.200 mm thick Interstitial Free (IF) steel whose composition is shown in Table 1.

The material is largely over-stoichiometric in Ti in order to completely stabilize the C and N in the form of TiC and TiN precipitates. Dog-bone shaped tensile coupons of IF steel with a gauge length of 5 mm, a width of 1 mm, and an average thickness of 0.197 mm were cut using electro discharge machining (EDM). Tensile coupons were then cleaned on both sides using ethanol followed by a 2 vol% Nital solution, and then rinsed using distilled water and ethanol. After the cleaning procedure, specimens were coated on both sides with an amorphous carbon-containing film (FeC) using physical vapor deposition (PVD). In addition to the deposition parameters already detailed in [4], pulses of methane were injected in the chamber to dynamically control the voltage between target and substrate which in turn controlled the carbon content in the film. The final carbon amount in the FeC film was 30 at% measured by Auger electron spectroscopy (AES) and by Atom Probe Tomography. At the end of the PVD process, 500 nm thick film were deposited on both sides of the IF steel substrate.

Another set of experiments was performed to investigate the influence of film thickness on carbon diffusion. Tensile coupons were coated on both sides using the PVD procedure illustrated above, with 50 nm, 100 nm, 200 nm, 300 nm and 400 nm thick FeC films.

2.2. Heat treatment

To investigate the diffusion of carbon from the film into the steel substrate, annealing treatments were carried out at temperatures of 330 °C, 430 °C, 530 °C, 630 °C, and 710 °C for 1 h in high vacuum (average pressure of 6×10^{-4} Pa). Specimens were heated inside a vacuum furnace at a heating rate of 12 °C/min until the target temperature was reached and held at that temperature for 1 h. The specimen was left to cool down inside the furnace with an initial cooling rate of 12 °C/min when the temperature was above 400 °C and then at 3 °C/min when the temperature dropped below 400 °C. Samples used to investigate the effect of film thicknesses were annealed at 530 °C for 1 h under high vacuum (average pressure 6×10^{-4} Pa).

To study the influence of the annealing environment, a series of tensile coupons were annealed for 1 h in an argon atmosphere at 530 °C and 630 °C, and others in air at 530 °C.

2.3. Mechanical properties

Tensile tests were carried out at a strain rate of $5\times10^{-4}\ s^{-1}$ on a minimum of three annealed coupons for a given temperature. For each test, yield stress, ultimate tensile strength (UTS), strain at fracture, Lüder's strain and Lüder's plateau length were obtained. For specimens showing Lüdering, the yield stress was taken as the upper yield stress, while for coupons without a plateau, the yield stress was taken as the stress at 0.2% engineering strain. The fracture surface of the tensile coupons was analyzed using scanning electron microscopy and the reduction in cross sectional area was calculated using the open-source image analysis software ImageJ [7].

Table 1
IF steel composition.

	C	Ti	P	Mn	S	N
$\times10^{-3}$ at%	14	64	16	113	22	7

Knoop hardness was measured to estimate the shape of the through-thickness carbon profile for the whole set of annealing temperatures (430 °C, 530 °C, 630 °C and 710 °C for 1 h). Knoop microhardness was preferred to Vickers since the depth of the indent is smaller for the same loading condition, which allowed for a better spatial resolution of the carbon profile. Knoop hardness was measured by applying a load of 100 g for 10 s. Before each hardness measurement, the specimen was polished to remove 20 μm, out of which 10 μm were removed using 4000 grit SiC paper, while the remaining 10 μm were removed using 3 μm, 1 μm and 0.05 μm polishing solutions. This procedure ensures no influence of polishing on the hardness results. After 20 μm were removed, Knoop hardness was performed again. The procedure was repeated until the center of the sheet was reached. For each hardness point, 15 Knoop measurements were recorded and the average hardness value was calculated discarding the two most extreme data points.

2.4. Transmission electron microscopy (TEM)

The microstructure of the coated IF coupon was characterized by Transmission Electron Microscopy (TEM) using an ARM200F JEOL microscope operated at 200 kV. Cross-section TEM samples were prepared using a focused ion beam (FIB; NVISION-40 Zeiss).

2.5. Atom probe tomography (APT)

Local composition measurements of the substrate material were carried out by atom probe tomography (APT) on samples prepared by FIB milling. Analyses were performed in ultra-high vacuum conditions, using an energy-compensated atom probe (EcoTAP CAMECA). Samples were field-evaporated using electric pulses (repetition rate 30 kHz and 20% pulse fraction) at 80 K. Six samples were selected for APT measurements. One uncoated and not annealed sample, two samples coated and annealed at 530 °C for 1 h and three samples coated and annealed at 710 °C for 1 h. For the annealed samples, one APT specimen was extracted from the middle of the steel substrate while the others were taken close to the film/substrate interface.

2.6. Thermo electric power (TEP)

To evaluate the amount of interstitial carbon in the samples after heat treatment, thermoelectric power measurements (TEP) were carried out. The set-up used for TEP measurements has been already described in the literature [8,9], and the protocol used for the present analyses was explained in detail by Lavaire et al. [10]. The protocol comprises a cold-rolling step (70%), which is performed to introduce a large amount of dislocations. Then, the TEP value of this cold-rolled state is assessed and the material is then aged (120 °C for 30 min) causing the segregation of all interstitial atoms at dislocations. After the ageing treatment, the TEP value is assessed again and the difference between this value and the value found after cold-rolling is related to the concentration of interstitial elements. TEP tests were carried out on coated IF steel after annealing for 1 h at 430 °C, 530 °C, 630 °C and 710 °C. For comparison, the same tests were also performed on uncoated IF steel.

3. Experimental results

3.1. Film characterization by transmission electron microscopy (TEM)

Transmission electron microscopy of the film before annealing reveals a fully amorphous structure as shown in Fig. 1 where the SAED pattern of the as-deposited FeC film only exhibits a typical diffuse halo. The film remains completely amorphous after annealing at temperatures up to 430 °C (see TEM analyses in Fig. 2), while films annealed at temperatures of 530 °C and higher are fully crystalline (see TEM analysis in Fig. 3). X-ray analyses performed using Co K-alpha radiation on FeC films after annealing at different temperatures confirmed that the crystalline phase is cementite (data not shown here).

The crystallization behavior of the FeC films used in this work is supported by results in literature for similar systems [11–13]. Crystallization of $Fe_{1-x}C_x$ films with $0.30 \leq x \leq 0.32$ has been studied using MÖssbauer spectroscopy by Bauer-Grosse and Le Caër [12,13]. They pointed out the presence of more complex mixtures of carbides whose carbon content varies continuously from $x=0.286$ (χ) to 0.31 and even 0.33 during the crystallization of sputtered FeC films [13]. In-situ TEM observations of the crystallization of similar FeC films obtained using the same PVD apparatus were performed by Fillon et al. [5]. In this study it was shown that 450 °C, the remaining amorphous film crystallizes into cementite, and in less than 3 minutes the film is completely crystallized. Annealed FeC films containing 30 at% of carbon have been analyzed using X-ray diffraction and the diffraction pattern confirmed that the film remains amorphous until 430 °C while at 530 °C it is fully crystallized into cementite [5]. The above results from the literature therefore suggest that at temperatures higher than 530 °C, film transformation is very fast and thus would occur before significant carbon diffusion can take place. This suggests that the amount of carbon available for diffusion into the IF steel substrate is determined by the excess of carbon present in the film after the film transformation into cementite (or other non- stoichiometric compositions close to that of cementite as shown in [13]).

3.2. Sample characterization by atom probe tomography (APT)

For specimens annealed at 710 °C, Ti and C rich precipitates were found in the middle of the sheet (Fig. 4), while these particles where not observed in the analyzed volumes for specimens annealed at 530 °C (Fig. 5). For specimens annealed at 710 °C other APT samples were analyzed closer to the film-substrate interface and Ti and C rich precipitates were found. The results are

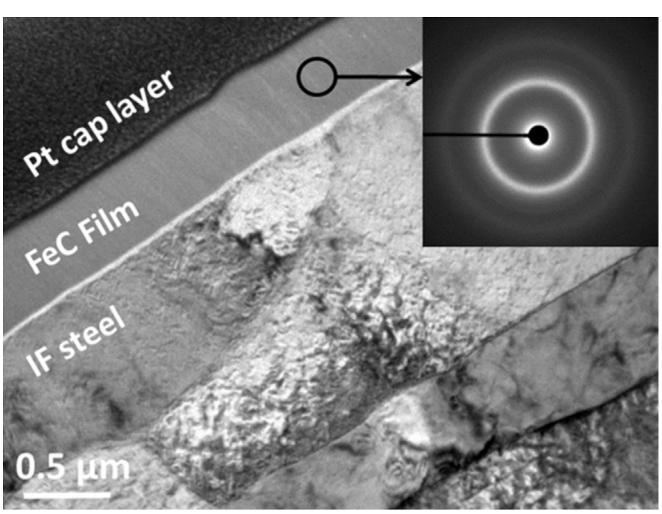

Fig. 1. TEM bright field image of the cross section of a coated IF steel coupon. The inset shows the Selected Area Electron Diffraction (SAED) pattern of the as-deposited FeC film. Only a diffuse halo corresponding to a non-crystalline phase is observed.

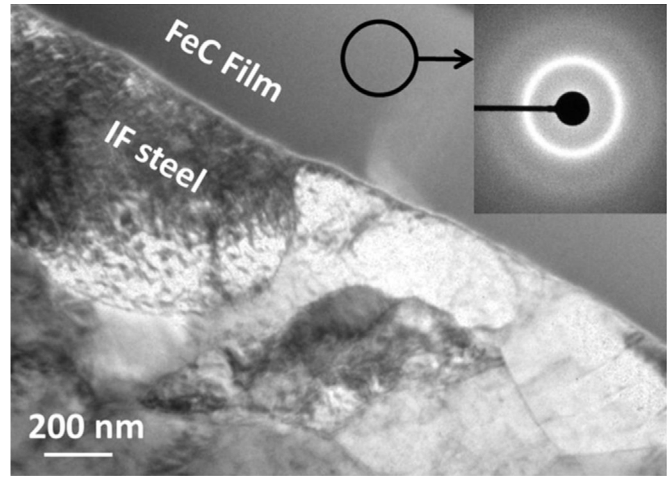

Fig. 2. TEM bright field image of the cross section of a coated IF steel coupon annealed at 430 °C – 1 h in high vacuum. The inset shows the Selected Area Electron Diffraction (SAED) pattern of the FeC film where the diffuse halo confirm the amorphous structure of the film.

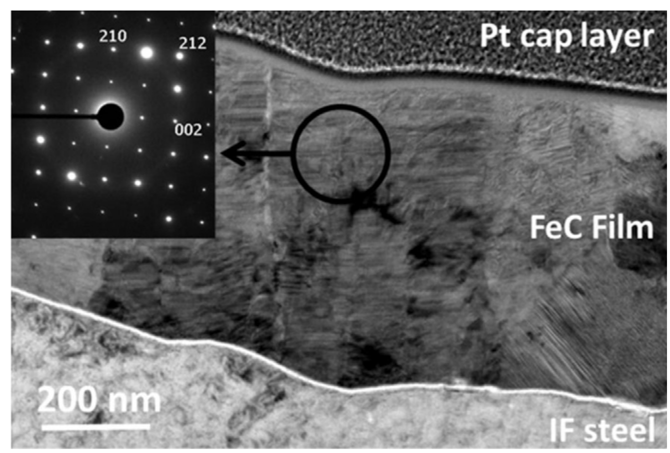

Fig. 3. TEM bright field image of the cross section of a coated IF steel coupon annealed at 530 °C – 1 h in high vacuum. The inset shows the Selected Area Electron Diffraction (SAED) pattern of the FeC film. The diffraction pattern confirm the crystalline nature of the film.

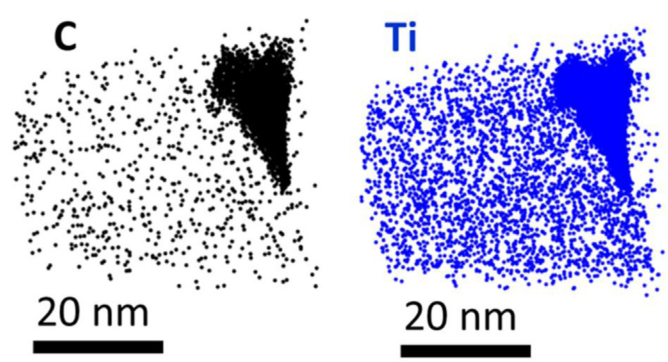

Fig. 4. Distribution of C and Ti atoms taken from the middle of the IF steel substrate for a specimen coated with a 500 nm thick FeC film annealed at 710 °C for 1 h in high vacuum (analyzed volume $48 \times 48 \times 70$ nm^3). Carbon and titanium contents in the precipitate are 24 ± 2 at% and 42 ± 2 at% respectively.

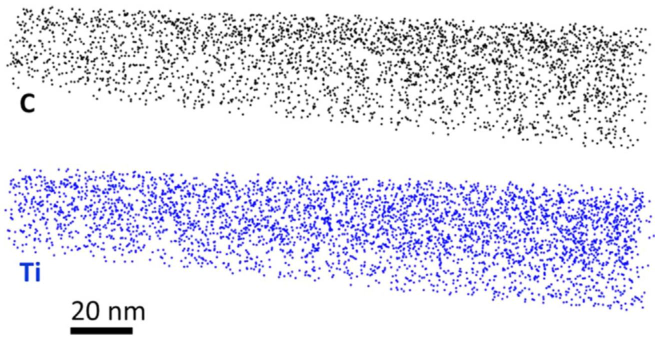

Fig. 5. Distribution of C and Ti atoms taken from the middle of the IF steel substrate for a specimen coated with a 500 nm thick FeC film annealed at 530 °C for 1 h in high vacuum (analyzed volume 41 × 41 × 210 nm^3). Carbon and titanium contents are 0.01 ± 0.01 at% and 0.06 ± 0.01 at% respectively.

summarized in Table 2. For the uncoated and not annealed IF steel, the carbon concentration is below the detection limit (50 ppm at.) but some Ti in solid solution was detected. Ti atoms were homogeneously distributed within the matrix and the measured composition was 0.04 at% (the value is quite close to the nominal composition of the IF steel sheet given by chemical analysis 0.064 at%, proving that most of the Ti atoms are not combined with carbon or nitrogen in the as-received IF steel).

These results demonstrate that the carbon initially present in the IF steel is completely stabilized by Ti. For specimens annealed at 530 °C/1 h, C atoms were detected in the analyzed samples and were homogeneously distributed within the matrix. The measured compositions of 0.02 at% C and 0.01 at% C in samples taken close to the film-sheet interface and in the middle of the sheet respectively, show C diffused into the IF steel substrate. At 530 °C, there is no significant evolution of the Ti distribution and no significant evolution of the Ti mean concentration in the matrix. For specimens annealed at 710 °C, carbon compositions measured within the matrix were lower than the values found for specimens annealed at 530 °C while a higher amount of carbon is expected to diffuse in the IF steel at 710 °C. The mean C concentration measured in the matrix for the sample taken close to the film-sheet interface and showing precipitation was 0.011 at% and no C atoms were detected in the matrix for samples taken in the middle of the sheet and showing precipitation. One should note that no quantifiable Ti was detected within the matrix for all specimens annealed at 710 °C, suggesting that the remaining Ti atoms initially present in solid solution have interacted with a part of the diffusing carbon to form or coarsen Ti and C rich precipitates, reducing the concentration of C atoms available to pin dislocations.

3.3. Thermo electric power (TEP)

To further support the results obtained from APT but on a

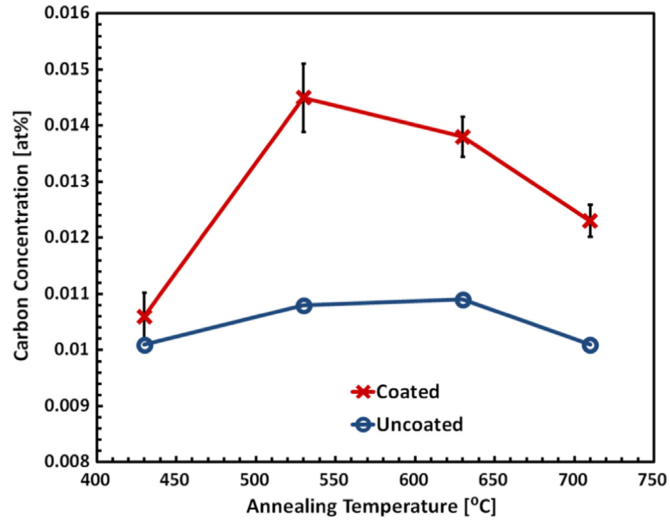

Fig. 6. TEP measurement results showing the average *C* concentration vs. annealing temperature for coated and uncoated samples.

macroscopic scale, thermoelectric power measurements (TEP) were performed to evaluate the amount of interstitial carbon in the samples as function of annealing temperature. As shown in Fig. 6, TEP values are constant for uncoated coupons since no carbon diffused into the IF substrate. On the contrary, for coated specimens, an increase in TEP was recorded with increasing temperature up to 530 °C, while the value remained roughly unchanged for annealing at 630 °C. However, at 710 °C a measurable drop in the TEP value was recorded compared to the value measured for annealing at 630 °C. It was calculated that the drop corresponds to 1.5×10^{-3} at% of interstitial C atoms which are not at dislocations anymore (thus not in solid solution in the specimens after annealing at 710 °C). From these results, it can be concluded that at 710 °C some of the carbon diffused from the FeC film to the IF steel matrix has probably precipitated.

3.4. Through thickness hardness profile

In order to quantify the through thickness carbon profile, sequential polishing followed by Knoop microhardness measurements were carried out and the results are presented in Fig. 7. The results show an increase in hardness with increasing annealing temperature except at 710 °C. It can also be deduced from the same figure that at temperatures equal or higher than 530 °C the hardness profile is constant through thickness, which implies a homogeneous carbon concentration. At 430 °C, a significant gradient of hardness can be observed from the outer surface towards the center of the steel, while a uniform carbon profile through thickness is obtained at 430 °C if the annealing is performed for 10 h.

Table 2
Summary of APT measurements performed on IF steel coated with a 500 nm thick FeC film.

APT Analysis	Fe (at%)		Ti (at%)		C (at%)		Notes
IF steel (uncoated and not annealed)	99.7 ± 0.01		0.04 ± 0.01		–		Sample taken from the middle of the sheet
Coated IF steel (high vacuum at 530 °C – 1 h) (*)	99.81 ± 0.01		0.06 ± 0.01		0.01 ± 0.01		Sample taken from the middle of the sheet
Coated IF steel (high vacuum at 530 °C – 1 h)	99.93 ± 0.01		0.01 ± 0.01		0.02 ± 0.01		Sample taken close to FeC – IF steel interface
Coated IF steel (high vacuum at 710 °C – 1 h)-first specimen (*)	**M**	**P**	**M**	**P**	**M**	**P**	Sample taken from the middle of the sheet
	99.82 ± 0.02	33 ± 2	–	42 ± 2	–	24 ± 2	
Coated IF steel (high vacuum 710 °C – 1 h)-second specimen	**M**	**P**	**M**	**P**	**M**	**P**	Sample taken close to FeC – IF steel interface
	99.94 ± 0.01	56 ± 4	–	24 ± 3	0.01 ± 0.01	10 ± 3	
Coated IF steel (high vacuum 710 °C – 1 h) – third specimen	99.89 ± 0.02		0.01 ± 0.01		0.02 ± 0.01		Sample taken from the middle of the sheet

* Indicates the volumes that are reconstructed in Figs. 4 and 5. M indicates the composition inside the matrix, while P indicates the composition inside the precipitate.

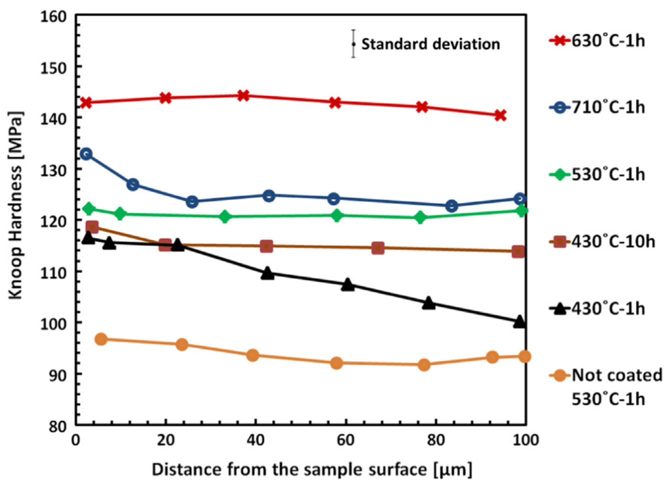

Fig. 7. Knoop hardness on specimens coated with a 500 nm thick FeC film annealed at different temperatures in high vacuum (the value 0 in the *x* axis corresponds to the coated and annealed surface, except for the reference uncoated sample).

3.5. Tensile tests

In Fig. 8, the engineering stress–strain curves for coupons coated on both sides with a 500 nm thick FeC film and annealed under high vacuum at different temperatures for 1 h are reported.

It can first be seen that before annealing, the FeC coating does not change the IF steel tensile behavior. At 330 °C no significant diffusion is occurring and the tensile curve is very close to the curve of a similarly coated reference sample before annealing. At 430 °C, an increase in yield stress is observed along with the appearance of a Lüder's plateau. Annealing at 530 °C and 630 °C for 1 h further increases both yield strength and ultimate tensile strength, while still showing a Lüder's plateau. At 710 °C, however, while a higher amount of carbon is expected to diffuse in the IF steel core, the measured yield strength and UTS are lower than the values found for specimens annealed at 530 °C and 630 °C. This is in agreement with the trend obtained from the hardness measurements.

Tensile tests were performed on uncoated IF steel annealed in high vacuum at 430 °C, 530 °C, 630 °C and 710 °C for 1 h. A comparison of the evolution of yield stress and UTS for coated and uncoated coupons annealed at different temperatures for 1 h in high vacuum is shown in Fig. 9. It was found that the yield stress is

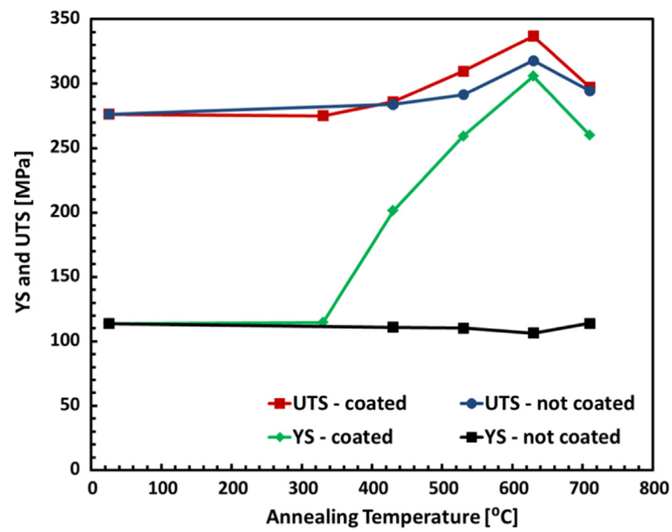

Fig. 9. Yield Stress (YS) and Ultimate Tensile Strength (UTS) for uncoated IF steel coupons and coated IF steel annealed in high vacuum at different temperatures for 1 h.

constant with increasing temperature for uncoated coupons while there is a large increase in yield stress for coated coupons starting at 430 °C due to carbon diffusion in the IF steel substrate. Coated and uncoated samples also show a difference in UTS which increases with increasing annealing temperature except at 710 °C. The origin of this behavior in the reference (uncoated) sample is not known.

3.6. Influence of film thickness

In Fig. 10, the engineering stress–strain curves for coupons having different film thicknesses and annealed at 530 °C are reported. A film thickness smaller than 200 nm is shown not to cause any change in mechanical properties. Above 200 nm, the thicker the film is, the larger is the increase in mechanical properties.

3.7. Influence of annealing environment

From Fig. 11, it can be seen that annealing in argon results in yield stresses and UTS slightly lower than those obtained in high

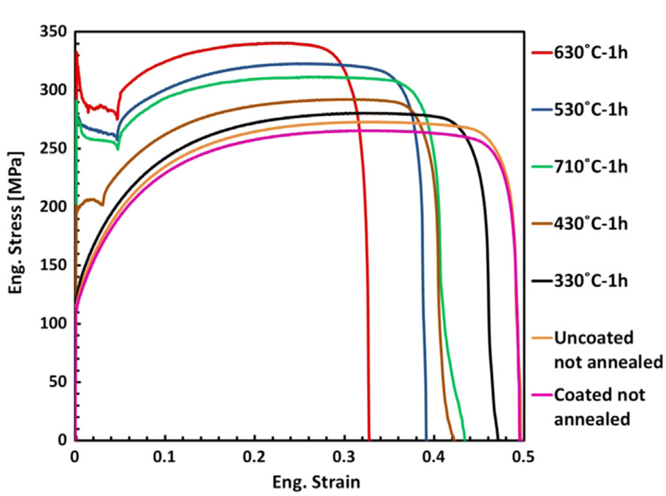

Fig. 8. Tensile tests results for coupons coated on both sides with a 500 nm thick FeC film and annealed at different temperatures in high vacuum.

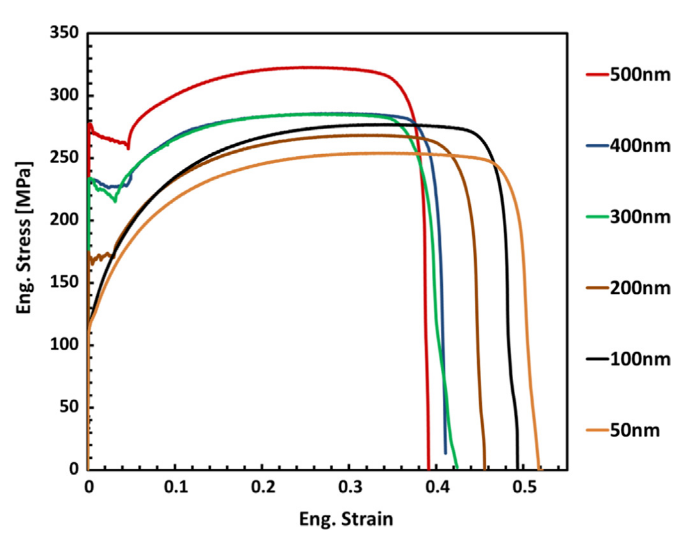

Fig. 10. engineering stress–strain curves for different FeC film thickness. Coupons annealed at 530 °C – 1 h in high vacuum.

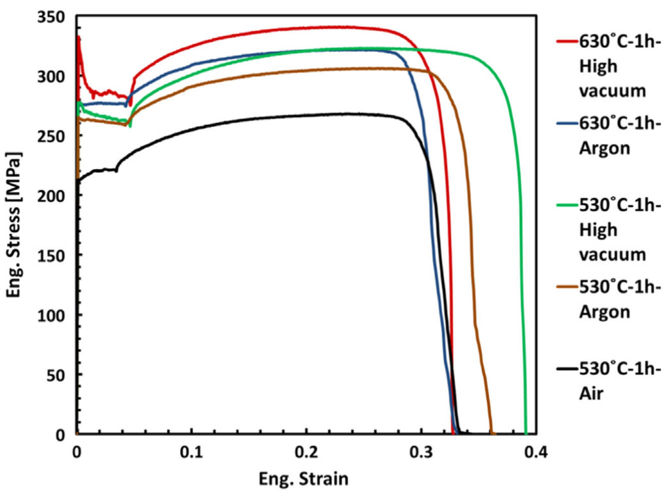

Fig. 11. Engineering stress–strain curves for coupons coated with a 500 nm thick FeC film annealed at 530 °C – 1 h under different annealing environments.

vacuum after annealing at 530 °C and 630 °C. It is probable that under the Ar atmosphere oxidation is taking place at 630 °C decreasing the amount of carbon diffusing towards the IF steel core. Indeed, argon of grade 5.3 was used which means that some oxygen (2 ppm) is present initially in the gas composition. This oxygen can then react with carbon from the FeC film and promote decarburization. In order to demonstrate film decarburization when oxygen is present, two specimens coated with a 500 nm thick FeC film were annealed in air at 530 °C – 1 h and the engineering stress–strain curve was compared with those of samples annealed in high vacuum and argon (Fig. 11). It is evident that diffusion of carbon is highly compromised when annealing in air because of the interaction of carbon with oxygen, so that very little carbon is effectively diffusing towards the substrate.

3.8. Fracture Surface

The fracture surface of the tensile coupons was analyzed using a scanning electron microscope to measure the area reduction at failure and evaluate damage resistance. The reduction in area for all specimens with a 500 nm thick film was found to lie in a range from 91.3% to 95.7%, while the reduction in area for specimens coated with different film thicknesses fell between 94.7% and 96.6%. Since the reduction in area is always greater than 90% even for specimens which have shown a significant improvement of strength, we can conclude that there is no significant variation in ductility. Moreover, applying the Considère criterion for thin sheets [14] on at least 2 specimens for each condition, it was found that the strain at necking is around 0.34 for not-annealed IF steel and for coupons annealed at 330 °C and 430 °C. At 530 °C and 710 °C, the strain at necking was slightly reduced to 0.29 which again confirms that even though the material is significantly strengthened, the uniform elongation remains high. A decrease of strain at necking was found for the coupons annealed at 630 °C.

4. Discussion

The results clearly demonstrate the ability to tailor the mechanical properties of IF steel sheets using physical vapor deposited carbon-rich films and diffusion annealing.

4.1. Carbon diffusion and strengthening model predictions

The through-thickness carbon profile expected for the different annealing temperatures was predicted by solving the 1-D general equation of second Fick's law (Eq. (1) [15]), where, $C(y, t)$ is the concentration at position y at time t, C_s is the concentration at the surface, and C_i is the initial concentration in the IF steel core. D is the diffusion coefficient of carbon in ferrite and L is the total length along which diffusion is happening. For our geometry, L is half the thickness of the tensile coupon since diffusion occurs from both sides of the coated IF steel.

$$\frac{C(y,t)-C_s}{C_i-C_s}=\frac{4}{\pi}\sum_{n=0}^{+\infty}\left(\frac{(-1)^{n+1}}{2n+1}\right)\times\cos\left(\frac{2n+1}{2}\pi\frac{y}{L}\right)\times\exp\left(-\left(\frac{2n+1}{2}\frac{\pi}{L}\right)^2 Dt\right) \quad (1)$$

The concentration of carbon in the coating is much higher than the solubility limit of carbon in ferrite, which is 0.1 at% at 727 °C according to the Fe–Fe_3C equilibrium phase diagram [16]. For this reason, as a first approximation, the carbon concentration in the film was assumed to be constant during diffusion. The boundary conditions used to model diffusion can be stated as follows: C_s (concentration at the surface) equal to C_{ss} which is the solubility limit of carbon into ferrite for the chosen annealing temperature for time t: $0 \le t \le +\infty$; $C_i=0$ initially for $t=0$ and through the whole thickness $-100\ \mu m < x < 100\ \mu m$.

The diffusion coefficient D was taken to follow an Arrhenius expression $D=D_0\times\exp(-Q/RT)$ where D_0 is equal to 0.0062 cm^2/s and the activation energy Q is equal to 80,350 J/mol [17]. Similar values for the coefficient D_0 and for the activation energy have been reported by McLellan and Wasz [18]. The solubility limit of carbon in ferrite (C_{ss}) is also changing depending on temperature and the following expression was used [17]:

$$C_{ss}=11.67\times\exp(-40600/RT) \quad (2)$$

Fig. 12 shows the results given by the model for carbon diffusion during an isothermal annealing of 1 h for five different temperatures taking into account heating and cooling profiles. From this modeling, it is expected that after annealing at 330 °C/1 h the amount of carbon diffused is negligible, while at 430 °C/1 h the carbon profile is expected to be non-uniform. Increasing the temperature to 530 °C, 630 °C and 710 °C causes higher diffusion of carbon in the sheet and the profiles are expected to be uniform and equal to the solubility limit of carbon in ferrite at those temperatures.

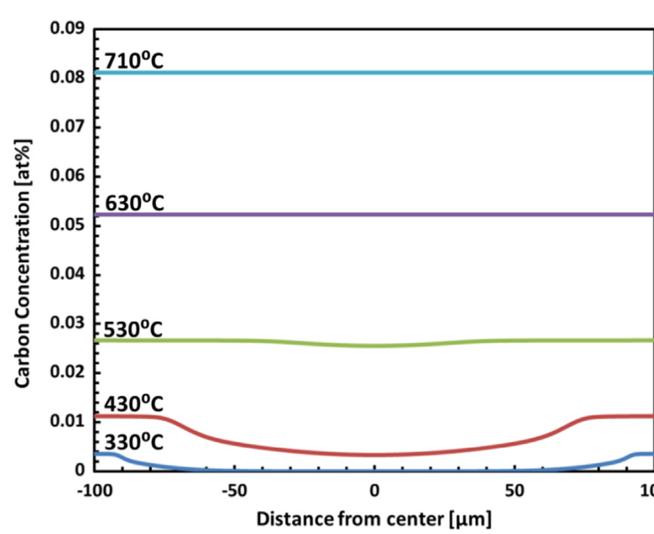

Fig. 12. Through thickness carbon profile predicted using the second Fick's law for coupons coated with a 500 nm thick FeC film.

The same model predicts that to obtain a uniform carbon profile at 430 °C, the specimen should be left at this temperature for 10 h. It is important to underline that the solubility limit used for carbon diffusion into ferrite is the one obtained from the Fe–Fe_3C equilibrium phase diagram; however, at temperatures below the coating crystallization temperature the ferrite is in equilibrium with an amorphous FeC film, so the solvus could in theory be different.

Carbon diffusion predictions shown in Fig. 12 are in good qualitative agreement with the experimental results up to a temperature of 630 °C. Indeed, both hardness and tensile test results (in terms of yield strength) show an increase in mechanical properties with increasing temperature which corresponds to an increase in carbon content as predicted by the model. Furthermore, the model was able to predict the non-uniform carbon profile through-thickness that was observed in the Knoop hardness results at 430 °C/1 h. At 710 °C, the model predicts that more carbon should diffuse into the IF steel substrate which should result in the highest hardness and strength levels. However, both hardness and tensile test results show a decrease in mechanical properties. This decrease will be discussed later in this section.

4.2. Strengthening model

The yield stress increase caused by the diffusion of carbon in solid solution was predicted using the following relation, [4,19]:

$$\Delta\sigma = Mm\sqrt{X_c} \tag{3}$$

where, X_c is the atomic fraction of carbon diffused in the substrate, M is the Taylor factor (M=2.5), and m is equal to 0.051μ (where μ=82 GPa is the shear modulus of the IF steel substrate). The average atomic fraction of carbon diffused through thickness can be predicted using a numerical solution of Eqs. (1) and (2) and the increase in yield stress can then be calculated using Eq. (3). As a first approximation it is assumed that only an amount of carbon equal to the classical solubility limit of carbon in ferrite at each isothermal temperature can be diffused in the IF steel core. In Fig. 13, the predicted yield stresses are compared with experiment for coupons coated on both sides with a 500 nm thick FeC film and annealed at different temperatures. The experimental yield stress values shown in Fig. 13 are averaged over three tensile coupons and the first experimental point at 25 °C represents the yield stress

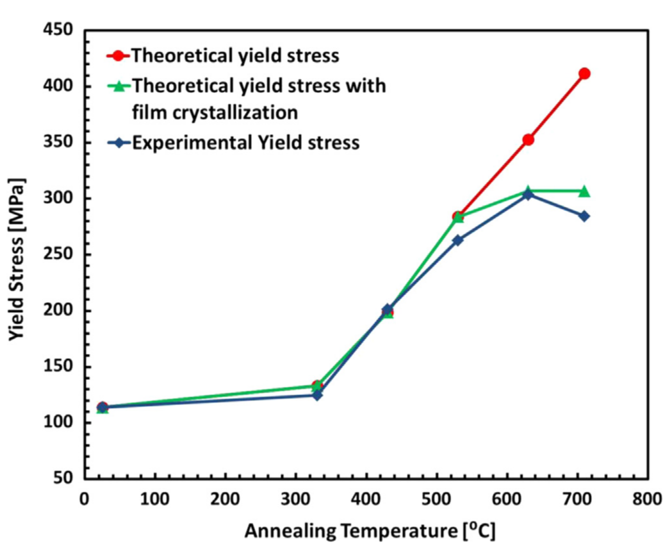

Fig. 13. Comparison between calculated yield stresses considering average carbon diffused inside IF steel predicted from the 1-D diffusion modeling, the yield stress obtained experimentally and the yield stress calculated considering the carbon available for diffusion after crystallization of a 500 nm thick FeC film.

for coupons coated but not annealed. As shown in Fig. 13 the predicted and experimental yield stresses are in good agreement up to 530 °C. At 630 °C and 710 °C, the increase in experimental yield stress is significantly smaller than what is theoretically predicted.

The smaller increase in yield stress at these two temperatures is attributed to the crystallization of the FeC film into cementite during heat treatment as discussed above. This crystallization limits the amount of carbon available to be diffused towards the IF steel substrate. Taking the stoichiometric composition of cementite (Fe_3C), with a film thickness of 500 nm on each surface of the IF steel coupon, it was found that the maximum amount of carbon available for diffusion after crystallization is equal to 0.0334 at%. This amount is higher than the solubility limit of carbon in ferrite at 530 °C, which explains why the mechanical properties are in agreement with predictions for this temperature. However, at 630 °C this value is lower than the solubility limit, which explains the lower yield stress found at this temperature. The increase of yield stress associated with this maximum carbon content that can be diffused (0.0334 at%) can be calculated using Eq. (3) and is equal to 191 MPa. Adding this amount to the average yield stress found during our experiments for a non-diffused IF steel (114 MPa) gives a total yield stress of 305 MPa which is in excellent agreement with the average stress (304 MPa) obtained from tensile tests (see Fig. 13). However, annealing at 710 °C – 1h shows a lower yield stress compared to the value of 305 MPa and the reason for this discrepancy is probably due to the coarsening (or nucleation) of Ti precipitates which lowers the amount of carbon in solid solution as shown by APT and TEP measurements. A discussion of the behavior after annealing at 710 °C is presented below.

4.3. Behavior at 710 °C

Both hardness and tensile test results show a drop of mechanical properties at 710 °C while APT and TEP results suggest the coarsening of carbides and a lower amount of carbon in solid solution. The type of precipitates present in Ti-stabilized Ultra-Low-Carbon (ULC) steels is very wide and includes TiN, TiS, $Ti_4C_2S_2$ and MnS, [2,20–22]. Based on this literature and on our APT and TEP results we suggest that some of the carbon diffused in the IF steel will interact with TiS particles to form or coarsen $Ti_4C_2S_2$ or will be used to form or coarsen TiC precipitates, considering that some titanium initially present in the IF steel is not combined with carbon. Since the interstitial carbon is used to form carbides, the level of solid solution strengthening (i.e. pinning of dislocations) decreases which in turns explains the lower mechanical properties observed at 710 °C. It should however be noted that not all carbon in solid solution will be used to form carbides since a Lüder's plateau can still be observed at 710 °C.

4.4. Influence of film thickness

To better understand the effect of film thickness on mechanical properties, stoichiometric calculations were carried out to evaluate the amount of carbon atoms still available to be diffused into the IF steel core at 530 °C after the film transformation into cementite. Fig. 14 shows the comparison between the yield stress calculated considering film crystallization and the experimental yield stress obtained for different film thicknesses. The error bars of the theoretical curve have been obtained by performing the stoichiometric calculation considering that the carbon content in the film has an uncertainty of ±3 at% from the nominal value of 30 at% and that there is an uncertainty of ±0.5 nm/min on the film thickness, with a deposition rate of 12 nm/min.

The calculated curve and the experimental curves are in good

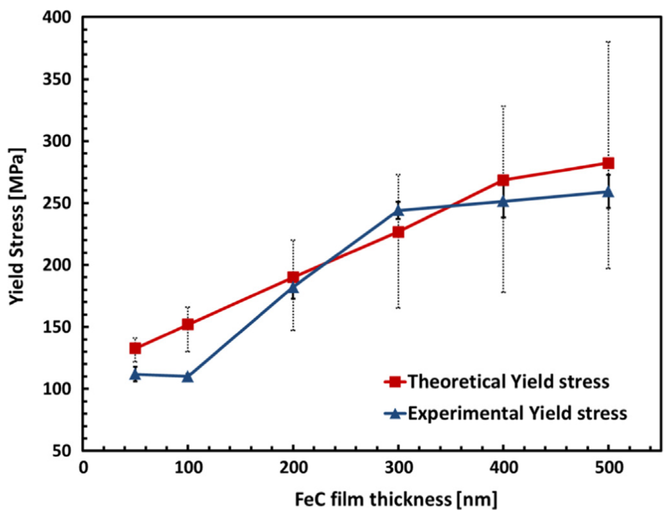

Fig. 14. Experimental yield stress obtained on coupons coated with different film thicknesses and annealed in high vacuum at 530 °C for 1 h and theoretical yield stress calculated considering crystallization of the FeC film into cementite.

agreement for thicknesses of film equal or higher than 200 nm. However for film thicknesses of 50 nm and 100 nm, the strength obtained experimentally is lower than expected. This could be due to a lower amount of carbon in the FeC film (probably even lower than 27 at%) and to thicknesses smaller than the required nominal values of 50 nm and 100 nm.

5. Conclusions

The results presented above have shown that FeC films can be used to introduce controlled carbon diffusion into steel sheets using temperatures lower than 800 °C with isothermal annealing times of 1 h. The increase in yield stress obtained experimentally was related to the amount of carbon diffused during annealing. The amount of carbon diffused into the IF steel sheet corresponds to the solubility limit of carbon in ferrite based on the Fe–Fe_3C diagram at the chosen annealing temperature, except for temperatures equal or higher than 630 °C where the solubility limit of carbon into ferrite is not reached because of the crystallization of the FeC film into cementite. All annealing temperatures (430 °C, 530 °C, 630 °C, and 710 °C) show an improvement in mechanical properties. However, at 710 °C/1 h the yield strength is lower than that obtained at 630 °C/1 h, since at 710 °C coarsening of Ti and C rich precipitates results in a lower amount of C in solid solution and thus in a decrease in mechanical properties.

The results presented in this paper have shown that the best mechanical properties are obtained by annealing under high vacuum and that annealing in Argon can also be used as a good alternative, while annealing in air should be avoided due to decarburization of the FeC film. It was also shown that it is possible to tailor the mechanical properties by varying the film thickness. For a 200 μm thick substrate, the coating thickness should be at least 200 nm in order to see an improvement in yield stress when annealing at 530 °C/1 h. Our results can be predicted using Fick's second law of diffusion provided that film transformation into cementite is taken into account.

The heat treatment performed during these experiments was a standard isothermal treatment of 1 h. It is believed that shorter thermal annealing at higher temperatures could be used to create a higher through-thickness gradient of carbon. The results obtained in this work offer a promising method to obtain higher strength interstitial free steels with no significant loss of ductility. These stronger IF steels could find applications in the automotive sector and could for instance be used to fabricate sandwich materials with lower density materials for structural applications where both weight savings and good bending stiffness are required.

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References

[1] F.C. Campbell, Elements of Metallurgy and Engineering Alloys, ASM International – The Materials Information Society.
[2] L. Baker, S. Daniel, J. Parker, Metallurgy and processing of ultra-low carbon bake hardening steels, Mater. Sci. Technol. 18 (2002) 355–368.
[3] S.R. Elmi Hosseini, Simulation of case depth of cementation steels according to Fick's laws, J. Iron Steel Res. Int. 19 (11) (2012) 71–78.
[4] C.P. Scott, C. Sinclair, A. Weck, "Amorphous $Fe_{1-x}C_x$ coatings as carbon reservoirs for diffusion strengthening of steel sheets,", Scr. Mater. 65 (2011) 763–766.
[5] A. Fillon, X. Sauvage, B. Lawrence, C. Sinclair, M. Perez, A. Weck, E. Cantergiani, T. Epicier, C.P. Scott, On the direct nucleation and growth of ferrite and cementite without austenite, Scr. Mater. 95 (2015) 35–38.
[6] D. Quantin, J.-L. Thirion, J.-J. Aernout, Sustainable development challenges for coated steel sheets, Revue de Metallurgie (2005) 315–322.
[7] W.S. Rasband, ImageJ, ⟨http://imagej.nih.gov/ij/⟩, 1997–2014.
[8] M. Perez, V. Massardier, X. Kleber, Thermoelectric power applied to metallurgy: principles and recent applications, Int. J. Mater. Res. 100 (10) (2009) 1461–1465.
[9] C. Capdevila, T. De Cock, F.G. Caballero, D. San Martin, C. Garcia de Andres, Application of thermoelectric power measurements to the study of cold rolled austenitic stainless steels, J. Mater. Sci. 44 (2009) 4499–4502.
[10] N. Lavaire, V. Massardier, J. Merlin, Quantitative evaluation of the interstitial content (C and/or N) in solid solution in extra-mild steels by thermoelectric power measurements, Scr. Mater. 50 (2004) 131–135.
[11] Robert Sinclair, Toshio Itoh, Richard Chin, In situ TEM studies of metal-carbon reactions, Microsc. Microanal. 8 (2002) 288–304.
[12] E. Bauer-Grosse, Thermal stability and crystallization studies of amorphous TM-C films, Thin Solid Films 447–448 (2004) 311–315.
[13] E. Bauer-Grosse, G. Le Caer, Crystallisation of amorphous $Fe_{1-x}C_x$ alloys (0.30.. x..0.32) and chemical twinning, J. Phys. F: Met. Phys. 16 (1986) 399–406.
[14] J. Gil Sevillano, Thin sheets story: plastic anisotropy, formability and strain localization, TECNUN, Materials Engineering.
[15] David S. Wilkinson, Mass transport in solids and fluids, Cambridge University Press.
[16] H. Okamoto, The C–Fe (carbon–iron) system, J. Phase Equilib. 13 (5) (1992) 543–565.
[17] V. Rebischung, C. Scott, Durcissement des Toles Minces par Revetements Carburisantes, USINOR Reserche et Developpement (CMC-IRSID).
[18] R.B. McLellan, M.L. Wasz, Carbon Diffusivity in BCC iron, J. Phys. Chem. Solids 54 (5) (1993) 583–586.
[19] M.J. Roberts, W.S. Owen, Solid solution hardening by carbon and nitrogen in ferrous martensites, The Iron and Steel Institute, Vols. Physical Properties of Martensite and Bainite-Special Report 93, pp. 1965, 171–178.
[20] M. Hua, C.I. Garcia, A.J. DeArdo, Precipitation behavior in ultra-low-carbon steels containing titanium and niobium, Metall. Mater. Trans. A 28A (1997) 1769–1780.
[21] J. Shi, X. wang, Comparison of precipitate behaviors in ultra-low carbon titanium stabilized Interstitial free steel sheets under different annealing processes, J. Mater. Eng. Perform. 8 (1999) 641–648.
[22] S. Carabajar, J. Merlin, V. Massardier, S. Chabanet, Precipitation evolution during the annealing of an interstitial-free steel, Mater. Sci. Eng. A281 (2000) 132–142.