Kinetics of Strain Aging in Cold Rolled Low Strength Multiphase Steel

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The kinetics of strain aging in cold rolled multiphase steel processed for a yield strength of 250 MPa and a tensile strength of 450 MPa (250/450 MPa grade of mechanical strength) was studied by means of aging experiments in the temperature interval from 50 to 185°C and time intervals ranging from 1 to 4,915 min followed by tensile tests.

The aging kinetics law was determined in terms of changes in the bake hardening value with the aging time and temperature for specimens with a tensile prestrain of 0.5%. The steel studied showed two strain aging stages, the first one between 50°C and 155°C (for times shorter than 9 min) and the second one between 125°C (for times longer than 211 min) and 185°C. The changes in the bake hardening value suggest, for the first stage, a process controlled by the locking of the dislocations in the ferrite due to the formation of clusters and/or transition carbides, such as the $\epsilon$-carbide, with an activation energy close to 70 kJ/mol and following a kinetic law with a time exponent of 0.4. In the second stage, the phenomenon is controlled by tempering of martensite, particularly the precipitation of transition carbides, $\epsilon$-carbide and/or $\eta$-carbide. The corresponding activation energy is approximately 130 kJ/mol and the kinetics of this stage can be described with a time exponent of 0.5.

KEY WORDS: multiphase steels; strain aging; bake hardening.

1. Introduction

The benefits in using conventional bake hardening steels (low and extra low carbon) for body applications in the automotive industry are well-known for several years.1–3) In general the industrially used bake hardenable (BH) effect is an aging phenomenon which is based on the diffusion of interstitial atoms in solid solution towards mobile dislocations. The dislocation mobility is therefore retarded or even suppressed and the yield stress is increased. It is also known for conventional bake hardening steels that a second stage of aging occurs after long aging times which is supposed to be controlled by precipitation effects on the dislocations. The dislocation mobility is therefore retarded or even suppressed and the yield stress is increased. It is also known for conventional bake hardening steels that a second stage of aging occurs after long aging times which is supposed to be controlled by precipitation effects on the dislocations. It is established that within a temperature range of 100–250°C, the carbide that precipitates from a supersaturated solid solution of carbon in bcc iron is hexagonal $\epsilon$-carbide.4)

Recently, advanced high strength steels with multiphase microstructures, consisting of ferrite, bainite, martensite and retained austenite have been developed which also show bake hardening properties.5,6) These materials are characterized by an interesting combination of high strength, good ductility, continuous yielding, high initial work hardening rates ($n$ values) and a low yield stress to tensile strength ratio (YS/TS). The bake hardening effect in multiphase steels is expected to be more complex in nature, due to its microstructure, and it is not yet fully understood. Recent investigations5,6) suggest that in addition to the contribution of solute carbon, further processes, in particular the tempering of martensite, play an important role in bake hardening of multiphase steels. According to literature,1,5–8) the microresidual stresses generated in the ferrite during quenching on account of transformation of austenite to martensite are relieved by the volume contraction that accompanies tempering, leading to an increase of yield stress. Therefore, several stages must be considered: (1) the Cottrell atmosphere formation in the ferrite, (2) the carbon-clustering and the precipitation stages in the ferrite, and (3) the effects owing to the tempering of the second constituent, mainly martensite. The strengthening stages are expected to overlap at higher aging temperatures.7)

In the present work the phenomenological and kinetic aspects of strain aging in cold rolled multiphase steel of the 250/450 MPa grade of mechanical strength were characterized by means of aging treatments and tensile tests.

2. Methodology

The steel used in this investigation was a laboratory cast cold rolled multiphase steel of 250 MPa yield stress and 450 MPa tensile strength grade. Chemical composition is shown in Table 1.
The steel was prepared as 50 kg ingot in an induction furnace operating under argon gas atmosphere. The ingot was cut into blocks of 35 mm thickness, which were reheated to 1250°C for 1 h and hot rolled in six passes to 7.0 mm thickness. The temperature of the coiling simulation was 650°C. The hot rolled sheets were machined and then cold rolled to a final thickness of 0.7 mm. The continuous annealing step was carried out in a GLEEble machine model 3500. The cycle used, shown in Fig. 1, was chosen taking into account the parameters adopted in the industrial line of continuous annealing. The annealed sheets were not temper rolled.

Metallographic samples of longitudinal sections of the blanks used in the continuous annealing step were prepared following standard metallographic procedures and examined by optical and scanning electron microscope. The volume fractions of the constituents were measured by image analyzer software. In order to determine the volume fraction of polygonal ferrite (PF) and of the second constituent, a 4% Nital etchant was used, while LePera etchant was applied to highlight the martensite/austenite (MA) constituent. The volume fraction of bainite plus undissolved carbides (B+C) was determined by the difference between the volume fractions of the second constituent and of the MA.

Tensile specimens with 25 mm gauge length parallel to the rolling direction were machined for the evaluation of the mechanical properties and of the kinetics of strain aging. To quantify the aging behavior, the specimens were then pretrained with a tensile strain of 0.5%, in an electromechanical INSTRON 5882 test machine, at a constant strain rate of $10^{-3}$ s$^{-1}$. A tensile prestrain of 0.5% was chosen because preliminary tests evidenced that this prestrain resulted in a maximum value of bake hardening index for aging at 170°C for 20 min. In order to avoid the possible occurrence of room temperature aging, pretrained specimens were stored in a freezer at $-20°C$.

Aging treatments were performed in a silicon oil circulating bath, at temperatures between 50°C and 185°C, aging times varying from 1 to 4915 min. Aged specimens were tensile tested at room temperature, under the same conditions used for prestraining. The aging kinetics law was determined in terms of changes in the bake hardening value with the aging time and temperature for specimens with a tensile prestrain of 0.5% ($BH_{0.5}$). The $BH_{0.5}$ value was determined by the difference between the lower yield stress after aging for a time $t$ at temperature $T$ and flow stress at the end of 0.5% of prestraining. In the case of the absence of a clear yield point, the 0.2% offset yield stress was used as lower yield stress after aging.

3. Results and Discussion

3.1. Microstructure and Mechanical Properties

As can be seen from Fig. 2, the steel showed a complex microstructure, consisting of a dispersion of bainite plus undissolved carbides and martensite/retained austenite particles in a polygonal ferrite matrix. The amount of different phases and the polygonal ferrite grain size (GS) are summarized in Table 2.

The mechanical property results for the as-annealed material are summarized in Table 3. Ten tensile specimens were prepared and tested in a Gleeble simulator.

| Table 1. Chemical composition of the multiphase steel used in the study (in weight percent). |
|------------------|--------|---|-----|-----|-----|-----|
| C                | Mn     | Si | P   | S   | Al  | Cr  |
| 0.062            | 1.56   | 0.02| 0.02| 0.0027| 0.018| 0.36| 0.0017|

| Table 2. Microstructural characterization of the investigated steel. |
|------------------|-------|-----|-----|
| MA (%)           | B + C (%) | PF (%) | GS (μm) |
| 5 ± 1            | 14 ± 1   | 81 ± 1 | 7.8 ± 0.5 |

Fig. 1. Continuous annealing cycle carried out in a Gleeble simulator.

Fig. 2. Microstructure of the studied steel. Scanning Electron Microscopy.
were analyzed and the error calculated, considering a Student’s t-distribution with a confidence level of 95%, was less than 2% for all parameters. In addition to a low yield stress/tensile strength ratio and high levels of uniform and total elongation observed in Table 3, it can be seen from Fig. 3 that the investigated steel exhibited continuous yielding behavior, which is caused by mobile dislocations produced at the ferrite/second constituent interfaces due to the volume expansion that takes place during transformation from austenite to martensite/bainite, on cooling from the quench temperature.9)

3.2. Static Strain Aging Behavior

The variation of \( BH_{0.5} \) value with the aging time and temperature is shown in Fig. 4. The steel studied showed two strain aging stages, the first one between 50°C and 155°C (for times shorter than 9 min) and the second one between 125°C (for times longer than 211 min) and 185°C. Figure 4 also shows that maximum \( BH_{0.5} \) values for the first and the second stages were estimated between 33 MPa and 37 MPa and 59 MPa and 63 MPa, respectively.

Waterschoot et al.7) also observed two strain aging stages for a dual phase steel containing 0.08% C, 1.50% Mn, 0.13% Si, 0.36% Cr and 0.21% Mo. The material studied, with 12% of martensite, was annealed at 780°C for 2 min and then fast cooled at the rate of 40°C/s to room temperature in an annealing simulator. After a certain period of time, the variation of the yield stress for specimens with a tensile prestrain of 0.5% (\( \Delta YS_{0.5} \)) increased to a saturation plateau of about 30 MPa, which is according to the results presented in Fig. 4. However, for the second stage, a maximum increase in the \( \Delta YS_{0.5} \) parameter of about 130 MPa was achieved. Bleck and Brühl3) and Byun et al.10) also observed the same behavior for dual phase steels. The increase in the \( BH_{0.5} \) value reached in the first stage by Bleck and Brühl3) was approximately 60 MPa. In the second stage, an increase was found in the \( BH_{0.5} \) of 100 MPa. The steel investigated by Bleck and Brühl3) contained approximately 20% of martensite. In the work of Byun et al.10) the first stage was observed for temperatures lower than 150°C, with a maximum increase in the yield stress of 35 MPa. In the second stage, observed between 170°C and 230°C, the increase in the yield stress was close to 50 MPa. The specimens analyzed, with 18% of martensite, were annealed at 720°C for 2 min and then fast cooled at the rate of 400°C/s to room temperature and then prestrained with a tensile strain of 2%. The difference observed between the values obtained for the present steel and the values reported in the literature3,7,10) mainly for the second stage, can be associated to the amount of martensite formed and also to previous tempering treatment carried out (260°C for 240 s, Fig. 1). According to Waterschoot et al.7), more martensite causes more internal stresses during transformation and a sufficient volume decrease during tempering afterward reduces these stresses significantly, yielding an increase of the yield stress. As verified by Chang,11) the effect of martensite in the increase of yield stress during the strain aging is reduced with the increase of the previous tempering temperature and time.

The kinetics of strain aging can be analyzed considering the Eq. (1),12) in which \( Y \) is the transformed fraction (aged fraction), \( k_2 \) is the rate constant, \( t \) is the time, and \( m \) is the time exponent.

\[
y = \frac{Y}{1 + k_2 t^m}
\]

Table 3. Longitudinal tensile properties.

| Property | Value (MPa) |
|----------|-------------|
| YS*      | 261 ± 2     |
| TS       | 501 ± 2     |
| YS/TS    | 0.52        |
| UEL%     | 22.9 ± 0.3  |
| TEL%     | 35.0 ± 0.4  |
| \( \eta_{0.2%} \) | 0.21 – 0.25   |

* 0.2% offset flow stress

a) Uniform Elongation
b) Total Elongation

Fig. 3. Stress–strain curves for investigated multiphase steel.

Fig. 4. Changes in \( BH_{0.5} \) value with time (min) at different aging temperatures.
The determination of the transformed fraction was accessed by means of the changes in $BH_{0.5}$ and $BH_{0.5,max}$ values, according to the Eq. (2).

$$Y = \frac{BH_{0.5,f}}{BH_{0.5,max}}$$ ...............................(2)

where $BH_{0.5,f}$ is $BH_{0.5}$ value measured at a given condition of time and temperature of aging and $BH_{0.5,max}$ is the maximum value reached by the $BH_{0.5}$ parameter at the same temperature.

The Eq. (1) can be rewritten as:

$$\ln \ln \frac{1}{1-Y} = m \ln k_v + m \ln t$$ ...............................(3)

When $\ln \ln \{1/(1-Y)\}$ is plotted against $\ln t$, as in Fig. 5, straight lines with $m$ as inclination and $m \ln k_v$ as intercept, should be obtained. Table 4 presents the values of the time exponent $m$ and $k_v$ calculated using the data shown in Fig. 5.

The rate constant $k_v$ in Eq. (1) is a function of the isothermal aging temperature according to the expression:

$$k_v = k_0 \exp \left( -\frac{\Delta H}{RT} \right)$$ ...............................(4)

where $k_0$ is a constant, $\Delta H$ is the activation energy of the phenomenon, $R$ is the universal gas constant and $T$ the absolute temperature. The activation energy, $\Delta H$, can thus be obtained from the inclination of the plot of $\ln k_v$ versus $1/T$.

Figure 6 shows the activation energy values obtained for the first and second strain aging stages, 68 ± 7 kJ/mol and 128 ± 11 kJ/mol, respectively.

The kinetics parameters $m$ and $\Delta H$ obtained for the first strain aging stage suggest a process controlled by the locking of the dislocations in the ferrite due to the formation of clusters and/or transition carbides, such as $\varepsilon$-carbide, for which it is expected, considering a process controlled by diffusion in a concentration gradient, a kinetic law with $t^{1/2}$.
and $\Delta H$ close to 70 kJ/mol. According to Zener, $m = 1/2$ for the growth of a plane front, provided the number of nuclei is constant. $\epsilon$-carbide forms as platelets on $\{100\}_\alpha$ planes once the clusters on the dislocations reach a critical size.

The mechanism influencing the difference in $m$ values obtained (0.36–0.39) and expected (0.5), considering a process controlled by diffusion in a concentration gradient is not well understood yet. However, it is possible that the cause of this discrepancy may be related to an inhomogeneous dislocation structure within the ferrite and high local mobile dislocation densities at the matrix/second constituent interface. In this case, the diffusion flux of the carbon atoms towards dislocations at interfaces would be unidirectional, that is, in the direction normal to the dislocations, which would lead to a time exponent equal to 1/3, as should be expected if cellular arrangements of dislocations were present in the material. It is also possible that the mechanism of movement of carbon atoms to the $\epsilon$-carbide interface is influenced by dislocation attraction and not only by diffusion in a concentration gradient, as mentioned above. According to Lement and Cohen, a dislocation attraction model predicts that the time exponent is 1/3. Whether these mechanisms, or possibly others, contributed to the observed time exponent results needs to be further investigated.

The value of activation energy obtained for the first stage is in good agreement with the activation energy reported by Byun et al. (71.06 kJ/mol) for the first strain aging stage in dual phase steel containing 0.07% C, 1.59% Mn, 0.03% Si and 0.06% Al for temperatures lower than 150°C. It is worth noticing that a process controlled by diffusion of carbon towards mobile dislocations in the ferrite, for the formation of Cottrell atmospheres, is characterized by values of time exponent of 0.67 and activation energy between 76 kJ/mol and 90 kJ/mol. According to De, Vandeputte and De Cooman, the apparent lowering of activation energy for the $\epsilon$-carbide precipitation process is difficult to interpret but it can be said that the $\epsilon$-carbide in the Fe–C system follows the path of minimum activation energy rather than that of maximum release of free energy. After the dislocations are saturated, the $\epsilon$-carbide precipitates grow along the $\{100\}_\alpha$ directions on individual dislocations which offers the path of minimum activation energy as the modulus of elasticity is minimum in $\{100\}$ directions in bcc iron.

Concerning the second strain aging stage, the value of activation energy obtained is in good agreement with the results reported by Waterschoot, Verbeken and De Cooman (123.8 kJ/mol) and Cheng et al. (111–126 kJ/mol) for the precipitation of $\eta$ and/or $\epsilon$-carbide, during the tempering of martensite, in the 120–195°C and 80–200°C temperature ranges, respectively. In an earlier study about the tempering of Fe–Ni–C martensite, it has been suggested that iron diffusion along dislocations could be the rate determining step for the precipitation of $\epsilon/\eta$-carbide. According to Cohen, the pipe diffusion of iron atoms is associated with an activation energy that can be compared with the values reported by Cheng et al. Such dislocations can be generated to accommodate the volume misfit between transition carbide and matrix (about 17% for the Fe–C alloy considered by Cheng et al.). In line with these results, a kinetic law with a time exponent of 0.5 also was obtained by Lement and Cohen for the formation of $\epsilon$-carbide during the tempering of martensite, based in a model controlled by diffusion in a concentration gradient acting alone. In this regard, it is important to note that the mechanism for the formation of $\epsilon$-carbide during the tempering of martensite is similar to that presented previously for the precipitation of $\epsilon$-carbide in the first strain aging stage. Therefore, due to values of time exponent and activation energy obtained, it is possible to associate the second strain aging stage of the investigated steel to the formation of transition carbides during the tempering of martensite in the 125–185°C temperature range.

4. Conclusions

The strain aging behavior of the investigated steel was characterized by two stages of increase of the $BH_{0.5}$ value with the aging time. For the first one, observed in the temperature range between 50°C and 155°C (for times shorter than 9 min), saturation $BH_{0.5}$ values between 33 MPa and 37 MPa were obtained. And for the second one, observed from 125°C (for times longer than 211 min) to 185°C, saturation $BH_{0.5}$ values between 59 MPa and 63 MPa were obtained.

The kinetics parameters $m$ (0.36–0.39) and $\Delta H$ (68±7 kJ/mol) obtained for the first strain aging stage suggest a phenomenon governed by the locking of the dislocations in the ferrite due to the formation of clusters and/or transition carbides, such as $\epsilon$-carbide, for which it is expected, considering a process controlled by diffusion in a concentration gradient, a kinetic law with $t^{1/2}$ and $\Delta H$ close to 70 kJ/mol.

The kinetic law determined to the second strain aging stage, with a time exponent of 0.5 and activation energy of 128±11 kJ/mol, is in good agreement with the values reported in literature for the precipitation of $\epsilon$ and/or $\eta$-carbide during the tempering of martensite in the 80–200°C temperature range.

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