DETERMINATION OF LOCAL CARBON CONTENT IN AUSTENITE DURING INTERCRITICAL ANNEALING OF DUAL PHASE STEELS BY PEELS ANALYSIS

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Abstract

Parallel electron energy loss spectroscopy (PEELS) has allowed to analyse and quantify local variations in the carbon concentration of austenite islands transformed during the intercritical annealing treatment of commercial dual-phase (DP) steels. These changes in the carbon content of different austenite regions are responsible for the different volume fraction of tempered martensite, martensite and retained austenite obtained after intercritical annealing and overaging treatment. This technique reveals how carbon distribution in austenite evolves as the transformation process advances.

Keywords: PEELS; Dual phase steel; Annealing; Overaging.

Introduction

Dual phase are essentially formed by a dispersion of martensite (10 to 40% volume fraction) in a ferrite matrix. Traditionally, they are produced by partial austenitisation followed by quenching. With the aim of reducing the significant difference in hardness existing between ferrite and martensite in the final microstructure of dual phase steels, the introduction of an overaging treatment has been recently evaluated [1-6]. It was found out that some austenite regions transformed to martensite during the cooling from the intercritical annealing temperature and were subsequently tempered as a result of the overaging treatment, rejecting carbon in form of fine carbides, which indicates that the martensite start temperature, $M_s$, of these areas was above the overaging temperature. Meanwhile, due to the fact that carbon is the alloying element that affects more strongly the values of $M_s$ [7-10] other austenite regions enriched in carbon had an $M_s$ value below the overaging temperature, so they transformed to martensite and/or austenite (MA constituents) during the quenching subsequent to the overaging. Thus, it seems that a non-uniform distribution of carbon in different austenite regions formed during intercritical annealing is obtained.

In the present work, transmission electron microscopy (TEM) associated with the technique of parallel electron energy loss spectroscopy (PEELS) was used for the accurate determination of the carbon concentration in austenite during intercritical annealing of dual phase steels. This study has revealed the existence of an inhomogeneous carbon distribution along different austenite islands that becomes more homogeneous with the evolution of the amount of transformation (%-Transf.) to austenite.

2. Experimental procedure
The dual phase steel investigated containing 0.15C, 1.9Mn, 0.2Si, 0.2Cr, 0.03Al and 0.015P (in wt.%), was elaborated using a 60kg vacuum induction furnace under inert atmosphere. Semi rolled slabs 30 mm thick were reheated at 1200°C for 45 min and hot rolled to about 3 mm in several passes finishing at 900°C. During the subsequent path the cooling rate was 60°C/s and the coiling was carried out at 500°C. After removing scale, samples were cold rolled by reduction in thickness of 68%.

Cold rolled samples were heated at a rate of 5°C/s to two different soaking temperatures (750 and 800°C) for different times (between 1 and 100s) and subsequently cooled at 100°C/s down to the overaging temperature. After aging at 270°C for 90 minutes, samples were gas quenched (cooling rate of 500 ºC/s, approximately). On the other hand, to analyse the local carbon content in austenite, cold rolled samples were intercritical annealed, eliminating the overaging treatment before gas quenching.

Quantitative data on carbon content in the austenite present in the intercritical annealed samples were obtained on a nanometre scale using a Philips CM200 FEG TEM/STEM microscope located at Arcelor Research (France). The microscope operating at 200kV was fitted with a Gatan 666 PEELS spectrometer controlled by the Gatan EL/P software (version 3.0). Thin foils for TEM examination were prepared using the conventional method of grinding to produce a 50 µm thin disc. These foils were dimple grinding to 20 µm, followed by electrolytic polishing at 16°C with a solution of 950 mL of glacial acetic acid and 50 mL of perchloric acid (65%) until perforation occurred, using a twin jet electropolisher set at a current of 0.1 A and a voltage of 60 V. To remove the surface oxide layers the perforated thin foils were further ion milled with a total current of 1 mA, an accelerating voltage of 3.5 kV and 10° incidences, for 10 minutes. Prior to analysis, thin foils were cooled down to -170°C in a Gatan 636 double tilt cooling stage to eliminate the build up of carbon contamination. Details of the technique used for carbon quantification by PEELS were reported elsewhere [11]. The PEELS scans used a probe size of 40 nm. The detection limit for carbon in this equipment is 0.04 wt.% and the relative error is of 3% in the carbon concentration range studied. The calibration procedure followed to test the precision of the PEELS quantification is described in detail elsewhere [11,12].

When using TEM associated with PEELS, it is impossible to distinguish austenite regions with different carbon contents. Since the analysis is carried out at cryogenic temperature, most of the regions of austenite formed during intercritical annealing were martensite at the analysis temperature (~-170ºC). Likewise, very small retained austenite islands were observed by TEM. The size is a parameter known to influence the austenite stability [12]. Thus, different martensite and austenite regions were selected for the analysis, always avoiding the presence of carbides near the areas where the carbon content was measured.

3. Results and Discussion

3.1. Characterisation of the influence of the carbon inhomogeneity in the final microstructure of dual-phase steels

As mentioned above, it is expected that the variations of the carbon concentration in different austenite regions induce the formation of a variety of phases in the final microstructure. Optical microscopy on overaged samples, corresponding with different amounts of transformation to austenite during intercritical annealing at 750 and 800°C, has shown the existence of several microstructural phases (Figure 1). In this Figure, the dark grey phases represent the tempered martensite in a clear grey ferrite matrix, while
the small white phases correspond with MA constituents that are rich in carbon. Moreover, it is possible to observe some isolated black carbides (usually in the ferrite matrix), which were formed during the cooling path from the hot rolling and were not dissolved during the intercritical annealing treatment. The quantity of these carbides decreases with the increase of the austenite volume fraction during the intercritical annealing treatment, as shown in Figure 1.

The quantification on optical micrographs of the volume fraction of MA constituents and tempered martensite present in the final microstructure has shown that the amount of tempered martensite was always much bigger than the volume of MA phases obtained during the quenching after the overaging treatment (Figure 2). Furthermore, results in Figure 2 suggest that the volume fraction of MA constituents decreases as the amount of transformation to austenite during intercritical annealing increases. Since the austenitisation is a diffusional process, in which the growth of austenite nuclei is controlled by the rate of the carbon diffusion [13], the volume fraction of carbon enriched austenite islands formed during partial austenitisation with values of $M_s$ below the overaging temperature, decreases with the advance of the transformation. Thus, this global decreasing of the carbon content in austenite is responsible for the small volume fraction of MA constituents obtained for high amounts of transformation. Hence, all these results seem to indicate the formation during the intercritical annealing treatment of austenite islands with different carbon concentrations, which inhomogeneity would be less severe as the amount of transformation goes on. This inhomogeneity in the carbon content of different regions of austenite induces a final microstructure formed by different quantities of MA constituents and tempered martensite.

Finally, TEM observations reveal some isolated retained austenite, corresponding with an amount of transformation to austenite of 40%, where its typical stacking faults can be seen [14, 15] (Figure 3). Moreover, some retained austenite associated with martensite was found in different samples (Figure 4).

3.2. Direct quantification of the carbon content in austenite by PEELS analysis

During local carbon quantification by PEELS it is important to avoid martensite areas with isolated undissolved carbides nearby that were formed after the hot rolling and cooling path because in this case the measured carbon content would be higher than the real content in austenite formed in the intercritical annealing. Numerical PEELS data are represented in Figure 5 as a distribution function of carbon content in different islands of austenite, depending on the amount of transformation reached during the partial austenitisation. For each austenitisation grade at least 100 different regions were analysed with a separation distance of 0.5 $\mu$m, approximately. These results confirm the existence of variations in the concentration of carbon between different regions of austenite formed during the austenitisation process. For austenite volume fractions between 0-50% the distribution was Gaussian-type and the inhomogeneity of the carbon content values was bigger than those obtained for higher amounts of transformation, where the distribution has been much more homogeneous. Carbide dissolution processes at the initial state of the transformation contribute to the high carbon content values detected in austenite at lower amounts of transformation. As the austenite grows, its carbon content distribution is centred in smaller values since the carbon inside the austenite after the dissolution of pearlite, assumed to be the eutectoid composition of the steel, soon will diffuse to the austenite/ferrite interface in order to re-establish the thermodynamic equilibrium at the corresponding temperature. Eventually, the values of carbon content in austenite tend to the nominal composition in the steel, as expected,
and the carbon inhomogeneity decreases as the amount of transformation advances and the transformation to austenite is completed. Thus, the most enriched in carbon austenite regions will not transform to martensite during the cooling from the intercritical annealing temperature, generating martensite and/or austenite constituents after the overaging treatment, as shown in Figures 3-4. Finally, these results obtained by PEELS suggest the existence of a considerable amount of austenite regions enriched in carbon (0.4-1.4 wt.%) during partial austenitisation for the typical amounts of transformation to austenite used in commercial dual phase steels (10-40% martensite volume fraction present in the final microstructure) [1]. Therefore, PEELS has demonstrated to be a useful technique with an excellent resolution to nanometrically measure the carbon content in austenite and to detect the existence of an inhomogeneous distribution in carbon along this phase in the annealed samples studied.

4. Conclusions

An inhomogeneous carbon distribution in different austenite regions formed during the intercritical annealing treatment of dual phase steels has been confirmed in this work. This inhomogeneity on carbon content was bigger for low amounts of transformation to austenite. The quantity of austenite regions with small carbon contents that generated tempered martensite in the final microstructure was always higher than the amount of austenite islands rich in carbon. As the austenite volume fraction grew, the average carbon content in austenite decreased and the carbon distribution became more homogeneous. The use of TEM associated with PEELS analysis has demonstrated to be a powerful technique to determine the carbon concentration on a nanometre scale in the austenite phase. Likewise, the study of the carbon distribution for different austenitisation grades has successfully explained the reason for the different volume fractions of tempered martensite, martensite and retained austenite, found in the final microstructures after the overaging treatment of dual phase steels.

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References

Figure Captions

Figure 1. Optical micrograph for different amounts of transformation to austenite during intercritical annealing: a) 10% (750 °C-1s), b) 30% (800 °C-1s), c) 40% (750 °C-20s), d) 80% (800 °C-20s). α- Ferrite, TM- Tempered Martensite, MA- Martensite and/or Austenite constituents. LePera etching (4% picric acid in ethanol mixed with a 1% solution of sodium metabisulfite in distilled water in a 1:1 volume ratio).

Figure 2. Volume fraction of MA constituents and tempered martensite, formed from austenite during intercritical annealing and overaging, as a function of the amount of transformation to austenite. Each amount of transformation corresponds to an intercritical annealing treatment: 10% (750 °C-1s); 30% (800 °C-1s); 40% (750 °C-20s); and 80% (800 °C-20s).

Figure 3. Thin foil TEM images of the steel with an amount of transformation to austenite of 40% (750 °C-20s): a) bright field image with small rounded carbides, square TiN particles and islands of retained austenite in a grey ferrite matrix, b) dark field image of an island of retained austenite with stacking faults.

Figure 4. TEM bright field and dark field images reveal austenite in MA constituents for an amount of transformation to austenite of: a) and b) 30% (800 °C-1s), c) and d) 80% (800 °C-20s). Larger magnification dark field images were chosen to highlight in detail the austenite regions.

Figure 5. PEELS data showing the evolution of the distribution of carbon content in austenite islands with the amount of transformation to austenite (%-Transf.). Each %-Transf. value corresponds to an intercritical annealing treatment: 40% (750 °C-20s); 50% (800 °C-5s); 60% (800 °C-10s); 70% (800 °C-15s); and 80% (800 °C-20s).