Ultrafine Grained Ferrite/Martensite Dual Phase Steel Fabricated by Large Strain Warm Deformation and Subsequent Intercritical Annealing

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An ultrafine grained (UFG) ferrite/cementite microstructure was produced by use of large strain warm deformation in two plain C–Mn steels. In order to overcome the characteristic restricted tensile ductility of this steel, an intercritical annealing was applied to obtain an UFG ferrite/martensite dual phase (DP) steel. Suitable intercritical annealing parameters have been worked out using dilatometry. Microstructure evolution during intercritical annealing has been investigated by means of scanning electron microscopy (SEM) and electron backscatter diffraction (EBSD). The study revealed that increasing the Mn content from 0.87 to 1.63 mass% was highly beneficial for the formation of martensite. This effect is explained by the enrichment of Mn in cementite which is partly inherited by austenite. The final microstructure consists of martensite islands embedded in an ultrafine grained polygonal ferrite matrix. The average grain size is 1–2 μm. Small amounts of retained austenite (<1 μm) are finely dispersed. The grain size is hardly affected by the intercritical annealing, whereas the fraction of high-angle grain boundaries in the ferrite matrix is reduced. Tensile tests revealed that strain hardenability is drastically improved by the introduction of martensite as a second phase. The UFG-DP steel exhibits a good combination of high strength and uniform elongation and considerable strain hardenability.

KEY WORDS: ultrafine grains; dual phase steel; Manganese; thermomechanical processing.

1. Introduction

Among the different processing routes to produce ultrafine grained steels, large strain warm deformation and annealing is an effective method to obtain ultrafine ferrite with finely dispersed spheroidized cementite. This steel exhibits high strength and toughness and fulfils the requirement for low production costs, being a plain 0.2%C–0.7%Mn–0.2%Si steel. Yet, the main drawback of ultrafine grained steels, the restricted tensile ductility due to a low strain hardening rate, has not been overcome. Besides other attempts, one approach to improve the strain hardenability and hence the industrial applicability is the introduction of martensite as a second hard phase into the soft ferrite matrix. The enhanced tensile properties of such dual phase steels can be associated with strain gradient plastic effects due to a high dislocation density in the interface area between martensite and ferrite. These dislocations are regarded as geometrically necessary dislocations. For these reasons, the aim of the present work is to transform the ultrafine grained ferrite/cementite (UFG F/C) steel into an ultrafine ferrite/martensite dual phase steel (UFG F/M DP) by intercritical annealing. The intercritical annealing is tested in two plain C–Mn steels, differing only in the Mn content. The parameters for intercritical annealing—heating rate, temperature and holding time—are settled such that a suitable ferrite grain size and martensite fraction is achieved.

2. Experimental Procedures

Table 1 shows the compositions of the two plain C–Mn steels and their reference names used in this work. The laboratory samples were machined directly from the cast ingot into rectangular parallelepiped samples of 50×40×60 mm³. The flat compression tests were conducted by use of a large scale 2.5 MN hot press at the Max-Planck-Institut für Eisenforschung. After 3 min austenitization at 934°C, a one-step deformation pass was imposed at 870°C in order to obtain fully recrystallized austenite. The flat compression tests were conducted by use of a large scale 2.5 MN hot press at the Max-Planck-Institut für Eisenforschung. After 3 min austenitization at 934°C, a one-step deformation pass was imposed at 870°C in order to obtain fully recrystallized austenite. This was followed by a controlled cooling procedure down to the pearlite finish temperature at moderate cooling rates (12 K/s) to obtain a bainite free ferrite–pearlite microstructure. The large strain warm deformation was performed by exerting a four-step flat compression series with an inter-pass time of 0.5 s. Each of the four subsequent deformation steps imposed a logarithmic strain of ε=0.4 at a strain rate of 10 s⁻¹. Subse-
An annealing treatment of 2 h at 550°C was applied. The resulting microstructure is an ultrafine grained ferrite matrix with homogeneously distributed spheroidized cementite particles which make up 2–3 vol% (Figs. 3(a) and 3(c)). Details of the thermomechanical treatment and the microstructure evolution during compression are described elsewhere.\textsuperscript{2)}

Intercritical annealing was tested on cylindrical samples with the gage of 4 mm×10 mm using a quenching- and deformation-dilatometer. The intercritical annealing temperature was set slightly above Ac\textsubscript{1}. For obtaining martensite, samples were quenched with hydrogen gas to room temperature. The cooling rate in the range between 730 and 500 °C, which is crucial for the later martensite formation was −140 K/s. In this way, a martensite fraction of 20–30 vol% was formed. Intercritical annealing of larger samples suitable for mechanical testing was performed in a salt-bath furnace. The complete processing route is depicted in Fig. 1.

Samples for SEM and EBSD investigations were prepared by standard mechanical grinding and polishing methods followed by etching in 1% nital. All microstructural investigations were carried out at sample locations where the local strain is equal to the nominal strain according to finite element calculations. The orientation mappings were performed using a high-resolution, high-intensity SEM with field emission gun. Phase fractions, grain sizes and grain boundary characters were determined by use of the EBSD orientation maps. Martensite and ferrite were distinguished by their different characteristic confidence index (CI) which is lower in martensite due to the higher degree of lattice imperfection. The grain size was determined using the mean linear intercept (MLI) method. Only high-angle grain boundaries (HAGB), commonly defined as boundaries between crystals having a misorientation above 15°, were counted in the analysis. Mn distribution in ferrite and martensite was qualitatively investigated by use of energy-dispersive spectrometry (EDS) attached to the SEM.

Mechanical properties were determined using flat tensile specimens with a cross section of 3.5 mm×5 mm and a gauge length of 10 mm. Tensile tests were conducted at room temperature with a constant cross head speed of 0.5 mm/min.

3. Results and Discussion

3.1. Determination of Intercritical Annealing Parameters

The ideal intercritical annealing parameters were established by performing dilatometer tests. The first aim was to determine the Ac\textsubscript{1} and Ac\textsubscript{3} temperatures that define the intercritical temperature range. Therefore, samples of both materials were slowly heated to 900°C, held for 2 min before cooling to room temperature. A low heating and cooling rate was chosen in order to experiment close to equilibrium conditions. Figure 2(a) shows exemplarily the result of one pre-test. Here, the temperature is plotted against the change in sample length. From these curves, the Ac\textsubscript{1} and Ac\textsubscript{3} temperatures were read. The results of several pre-tests are shown in Fig. 2(b). For comparison, the equilibrium Ae\textsubscript{1} and Ae\textsubscript{3} temperatures were calculated for a range of Mn contents using Thermo-Calc.\textsuperscript{13)} It can be seen that the equilibrium and experimental values are in quite good agreement and that they show the same decreasing tendency with increasing Mn content. The temperature shift is due to the fact that Mn is an austenite stabilizer and hence, lowers the Ac\textsubscript{1} and Ac\textsubscript{3} temperatures. The equilibrium temperature for the desired austenite fraction of 30 mass% is 742°C for the 16C steel and 712°C for the 17C–Mn steel, respectively. To set the intercritical annealing temperature properly, two facts must be taken into account: 1) Equilibrium conditions can not be reached during the experiments. 2) The mismatch between calculated and measured values is higher in the case of the 17C–Mn steel. Considering these informa-

![Fig. 1. Complete processing route for the production of ultrafine grained ferrite/martensite dual phase steel.](image-url)

![Fig. 2.](image-url)

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The intercritical annealing temperature was chosen to be 750°C for the 16C steel and 730°C for the 17C–Mn steel.

Figure 3 shows the first results, obtained by intercritical annealing at 730°C for 3 min. In the left column, the UFG F/C steels fabricated by large strain warm deformation are presented, and in the right column, the same samples after intercritical annealing. The UFG F/C microstructure is similar in both materials, yet, in the 16C steel, the grain size is slightly larger and the cementite fraction slightly lower. It is obvious that during intercritical annealing, phase transformation has happened in both materials. In the 17C–Mn steel, the whole austenite has transformed into martensite, except from minor amounts of retained austenite that are not visible in the SEM images. However, the austenite in the 16C steel only partially transformed into martensite. The remaining austenite has undergone reconstructive transformation into pearlite. Furthermore, considerable grain growth has happened in the 16C steel. This is partially due to the higher intercritical annealing temperature required for this steel and partially to a smaller amount of cementite particles in the initial microstructure, which are responsible for the pinning of the grain boundaries. As the only difference between the materials is the Mn contents, the reason for this unlike behaviour must be found in the Mn distribution, as will be described in Chap. 3.3. As it was impossible to obtain a ferrite/martensite dual phase structure in the 16C steel with the applied technique, the following investigations were performed exclusively on the 17C–Mn steel.

3.1.1. Influence of Holding Time

After the intercritical annealing temperature had been settled, a convenient holding time to achieve the desired martensite fraction had to be found. Figure 4 shows two samples of the 17C–Mn steel after large strain warm deformation and intercritical annealing, imposing a holding time of 2 s (a) and 10 min (b) before quenching with hydrogen gas. MLI, mean linear intercept length.
2 s, there are some cementite particles visible that have not yet transformed, whereas in the sample held for 10 min, martensite fraction is largely above 30% which will be harmful to ductility. Furthermore, the martensite islands are mostly interconnected parallel to the rolling direction. These martensite bands are preferred locations for crack propagation and are therefore disadvantageous for later applications. By varying the holding time in the range from 2 s to 10 min, it was found that a holding time of 1 min was sufficient to transform all cementite and to achieve a martensite fraction in the desired range. Therefore, a 1 min holding time was chosen for the following investigations.

It should be noted, that the ferrite grain size does not increase significantly due to a longer heat treatment. The mean linear intercept (MLI) length was 1.6 μm after 2 s holding time and 1.8 μm after 10 min holding time. This point indicates that grain boundaries are effectively pinned by the carbides and in the following by the austenite transformation. Therefore, grain growth is strongly inhibited. Comparing Figs. 4(a) and 4(b) the misleading impression could arise that the grain size is much larger in the right image than in the left one. However, one must consider that the grain size analysis was made on the basis of EBSD maps, not on the depicted SEM images. In Fig. 4(a), a lot of submicron carbides are visible as well as subgrains in the ferrite. Both are not included in the grain size determination.

3.1.2. Influence of Heating Rate

The last parameter to be settled is the heating rate. As for different industrial processing routes defined heating rates are required, it is of practical interest to investigate to what extent the heating rate up to the intercritical temperature affects the microstructure. Figure 5 shows the microstructures of two samples (17C-Mn steel) heated with a rate of 0.25 K/s (a) and 100 K/s (b).

It is obvious that the heating rate does not influence the phase transformation and hence, the martensite fraction is almost equal in both samples. Yet, the grain size is slightly larger in the slowly heated sample. To avoid grain growth during heating, a rapid heating is preferable, but not crucial. Therefore, an intermediate heating rate of 20 K/s was chosen as a standard for the following investigations.

3.2. Characteristics of the Final Microstructure

The obtained microstructure consists of 25% martensite and has an average ferrite and martensite grain size of 1–2 μm. The ferrite matrix exhibits a strong (110) || RD rolling texture, which does not change noticeably during intercritical annealing. The martensite islands or packets are subdivided into blocks of different orientations. The blocks are separated mostly by high-angle grain boundaries (Fig. 7(c)). Their size ranges from 1 μm to 50 nm, which is close to the spatial resolution of the SEM. Beside ferrite and martensite, small amounts (2–4 vol%) of retained austenite build up the microstructure. Its grain size varies from 0.1 to 1 μm, a diameter of 0.5 μm being most common (Fig. 7(c)). The retained austenite appears partly as isolated grains, partly it is attached to martensite.

Figure 6 shows the grain boundary character distribution before (a) and after (b) the intercritical annealing.
6(b) by the empty black bars) leads to a distribution very close to the one of the UFG F/C steel (Fig. 6(a)). It must be added that here, only the interface boundaries between ferrite and martensite are included in the distribution curve, but not the inter-block boundaries of the martensite substructure.

3.3. Effect of Mn Distribution on Microstructure Evolution

Figure 7(a) shows the gray scale Image Quality (IQ) map of the 17C–Mn steel after intercritical annealing, heated with 20 K/s to 730°C and held for 1 min. The martensite, the retained austenite and the grain boundaries appear dark due to higher lattice imperfections compared to the recovered ferrite. Figure 7(b) shows the distribution of Mn in a semi-quantitative way. The colour band from white to black displays an increase of the local Mn concentration (the unit is X-ray counts). In Fig. 7(c), the corresponding grain boundary map is shown, including the locations of retained austenite.

It was shown in a previous project\(^{14}\) that Mn is advantageous for the production of ultrafine grained ferrite/cementite steels using large strain warm deformation. An increase in Mn content from 0.74 to 1.52 mass%, which is very close to the present investigation composition (0.87 and 1.63 mass%), decreases the average ferrite grain size, increases the fraction of HAGB and leads to a lower aspect ratio. These effects were explained by the enrichment of Mn in cementite which forms Mn–Fe carbides that are characterized by a higher stability compared to the Fe carbide.\(^{15}\) The high stability leads to a finer distribution of these particles and hence, to a higher fraction of effectively pinned grain boundaries. Furthermore, the high-Mn carbides are more resistant to Ostwald ripening.

It is well known, that the nucleation of austenite from ferrite/cementite structures starts at the interface between both phases.\(^{16,17}\) Therefore, the Mn-enrichment in cementite is of particular importance for the intercritical annealing applied in this study. As one can see from Fig. 7(b), Mn is enriched in both martensite (encircled area) and retained austenite (square) compared to the ferrite matrix. Local maxima in Mn counts can be attributed to both martensite and austenite. Some larger martensite packets do not show the characteristic Mn enrichment. This is probably due to dilution effects occurring during the growth of austenite into the ferrite matrix. The observations imply that Mn enrichment in cementite, which has been documented before, is passed on to the austenite and in the following to the martensite. It is known that Mn enhances the hardenability and therefore lowers the critical cooling rate for the martensite formation. The high Mn concentration in the austenite could be the reason, why at the present cooling conditions (−140 K/s), martensite was obtained only in the 17C–Mn (1.63 mass% Mn) steel, but not in the 16C (0.87 mass% Mn) steel. In the latter, the Mn concentration is not sufficient to cause an efficient Mn enrichment in cementite which can be passed on the austenite.

3.4. Mechanical Properties

The intercritical annealing of the tensile test specimen was performed in a salt-bath furnace. Here, the average heating rate was 8 K/s and the specimen were held at 730°C for 1 min. Figure 8 shows the engineering stress–strain curves of the 17C–Mn steel after large strain warm deformation with and without subsequent intercritical annealing.
features of UFG metallic materials; high yield strength, pronounced Lüders strain and a very low strain hardening rate, leading to a high yield ratio of $\frac{\sigma_y}{\sigma_{UTS}} = 0.9$. Early necking and large reduction in area are further characteristics that are documented clearly in our current data.

With the introduction of martensite as a second phase, the tensile behaviour changes drastically. The UFG F/M DP steel is characterized by a lower yield strength, continuous yielding, a high initial strain hardening rate and a high ultimate tensile strength, resulting in a low yield ratio of 0.5. The reduction in area (RA) is smaller, as it is typical of DP steels. The very high initial strain hardening rate combined with a significant increase of the flow stress leads to a limited increase in uniform elongation in comparison to the UFG F/C steel. As the tensile tests were not conducted in accordance with the ASTM standards, no reliable values for the total elongation can be given. Yet, the characteristic difference between both curves is evident.

The absence of discontinuous yielding is probably caused by the introduction of additional mobile dislocations during the austenite–martensite transformation. A high dislocation density in the martensite–ferrite boundary area was documented by Park et al.\textsuperscript{7}) In the present study, the retained austenite could have an additional positive effect on the strain hardenability by providing fresh dislocations due to the martensite transformation during straining. Further investigations are needed to prove the contribution of retained austenite to strain hardening.

4. Conclusions

(1) Large strain warm deformation and subsequent intercritical annealing is an efficient method to produce ultrafine grained ferrite/martensite dual phase steel.

(2) It turned out that a Mn content of 1.63 mass% in comparison to 0.87 mass% is highly beneficial for the formation of martensite during quenching. This is due to the Mn enrichment in cementite which is partly inherited to the austenite that undergoes martensite transformation.

(3) The fraction of high-angle grain boundaries in the ferrite matrix is reduced during intercritical annealing. Yet, it is balanced by the high-angle ferrite–martensite grain boundaries.

(4) The ferrite grain size is largely stable during intercritical annealing and is rarely sensitive to intercritical heating rate and holding time.

(5) The strain hardening rate is drastically improved by the introduction of martensite as a second phase. Continuous yielding and a high ultimate tensile strength are probably a result of mobile dislocations in the martensite–ferrite boundary area. Small amounts of retained austenite might further enhance strain hardenability.

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| Steel       | $\sigma_y$ [MPa] | UTS [MPa] | yield ratio | $\varepsilon_u$ [%] | RA [%] |
|-------------|-----------------|-----------|-------------|---------------------|-------|
| UFG F/C     | 589             | 665       | 0.89        | 10.6                | 65    |
| UFG F/M DP  | 452             | 893       | 0.51        | 11.3                | 31    |