Experimental report

03/10/2024

Proposal: 1-01-199 **Council:** 4/2023

Title: Effect of C content on microstructural stability of retained austenite in martensitic microstructures during tempering

Research area: Materials

This proposal is a new proposal

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Samples: Steels with C content ranging from 0.2 to 1wt%

Instrument	Requested days	Allocated days	From	To
D1B	2	2	11/09/2023	13/09/2023

Abstract:

The effect of carbon content on microstructural stability of retained austenite in martensitic microstructures will be studied in 8 steels with carbon content ranging from 0.2 to 1%C. These microstructures have been developed by a thermal treatment consisting of austenitization at 1000ºC from 3 min followed by quenching to room temperature at 100ºC/s. Neutron diffraction measurements will be performed during a heating and cooling cycle between 20 and 975ºC at 8ºC/min. These data will be correlated with XRD patterns obtained on samples heated to a given temperature at the same rate and then quenched at RT. We expect from this combined analysis to determine: the actual amount of austenite at a given temperature, the temperature interval for the highest carbon enrichment of the austenite to optimize quenching and partitioning treatments, and verify the existence of an auto-temepering process during cooling to room temperature. Finally, the limitations and range of application of the most widely used methods (dilatometry and interrupted tempering tests) will be evaluated to determine the optimal conditions for steel processing.

Proposal 1-01-199: "Effect of C content on microstructural stability of retained austenite in martensitic microstructures during tempering"

1. Objectives:

This proposal aims to study the stability martensitic microstructures during the tempering of steels with a C content of up to 1 mass% and to analyze the effect of different alloying elements. For this goal, neutron powder diffraction (NPD) patterns recorded in situ in the D1B diffractometer during a heating and cooling cycle between 20 and 975ºC at 7.5ºC/min will be correlated with the X-ray diffraction (XRD) patterns obtained in samples heated up to a given temperature at the same rate and then quenched to room temperature (RT). This study will allow us to evaluate the limitations and the range of application of the most widely used methods (dilatometry and interrupted tempering tests) to determine the optimal heat treatment conditions for steel processing.

2. Samples analyzed:

3 samples containing 0.4, 0.5, 0.8 %C (samples 04C3Si, 05CV and SP10) and 2 samples containing 1%C but different alloying element contents (samples Aus 2 and 1CMo) have been austenitized at 1000ºC for 180 s and then quenched to room temperature at 100ºC/s to develop a martensitic microstructure.

3. Measurements performed:

The following measurements have been performed on the D1B diffractometer using λ= 1.28Å on the different samples:

a) Sample 04C3Si: After taken reference diffraction patterns at RT during 15 min, the sample was heated up to 950ºC at a heating rate of 7.5ºC/min. The sample was stabilized at 950ºC and then was cooled down to RT at 7.5ºC/min. Both, the heating and cooling processes were monotorized by recording a ND pattern every 2 min. In total, 119 frames were obtained.

b) Sample 05CV: After taken reference diffraction patterns at RT during 15 min, the sample was heated up to 950ºC at a heating rate of 7.5ºC/min. The sample was stabilized at 950ºC and cooled down cooled down to 200ºC at 7.5ºC/min. This heating and cooling cycle was repeated so that 403 frames were obtained.

c) Sample SP10C: After taken reference diffraction patterns at RT during 15 min, the sample was heated up to 950ºC at 7.5ºC/min. After stabilizing the temperature a 950ºC, the sample was cooled down to 240ºC at 7.5ºC/min. This heating and cooling cycle was repeated, so that 481 frames where collected.

d) Sample Aus 2: After taken reference diffraction patterns at RT during 15 min, the sample was heated up to 950ºC at 7.5ºC/min. After stabilizing the temperature a 950ºC, the sample was cooled down to 125ºC at 7.5ºC/min. In total, 145 frames were recorded

d) Sample 1MoC: After taken reference diffraction patterns at RT during 15 min, the sample was heated up to 950ºC at 7.5ºC/min. After stabilizing the temperature a 950ºC, the sample was cooled down to 340ºC at 7.5ºC/min. In total, 82 frames were recorded

e) These measurements were complemented with the measurement at room temperature of standards of Si and Na2Ca3Al2F14 to determine the precise wavelength value and to parameterize empirically the instrument functions from their profile shape analysis, respectively.

4. Results appreciated in-situ in ILL from the evolution of recorded diffractograms:

A first check of the NPD patterns recorded at room temperatures showed:

a) X-ray diffraction patterns revealed splitting in martensite reflections only for SP10, Aus 2 and 1MoC samples. A close examination of the Bragg reflection of these patterns led to the conclusion that the reflection intensity ratio of reflection doublets (002)/(200) and (112)/(211) is lower than the theoretical intensity ratio, which is assumed to be 0.5 based on the ratio multiplicities of these reflections On the other hand, simulated diffraction patterns obtained using the Rietveld refinements of the NPD data showed a slight shift of the (002) and (112) lines towards greater angles, leading to lower values of the lattice parameter c. Thus the c/a ratio of these samples correspond to an average C content in solid solution lower than the alloy's nominal C concentration. Besides the shape of the martensite peaks cannot be reproduced correctly when the double Voigt approach is used for the line broadening analysis. These three facts are shown in Figure 1 for the SP10 alloy. They may be related to two colonies of martensite each with different C content in solid solution, and therefore with a different c/a ratio. When the martensitic transformation begins at high temperature, the C within the first martensite formed can make some atomic jumps before freezing within this phase. The short-range motion of C to dislocations, lath boundaries, grain boundaries, and other lattice defects (auto-tempering effect) through the martensite temperature range, causes that the true C content inside this martensite is close to that of the tempered martensite.

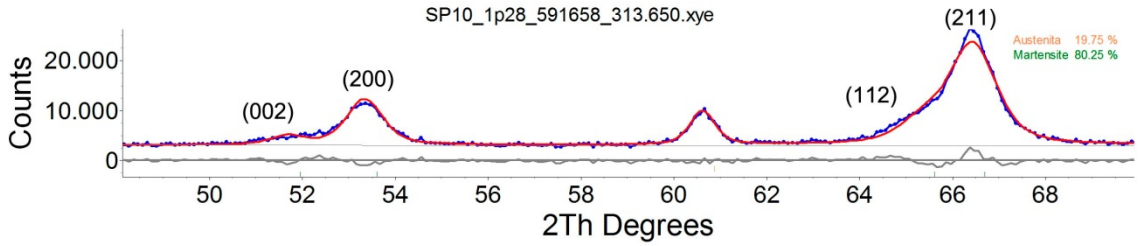

Figure 1 Results of Rietveld refinements of the NPD patterns recorded at RT for the SP10C sample. The differences between experimental data (blue line) and the fitted simulated pattern (red line) are plotted as a continuous black line at the bottom.

b) Splitting of martensite reflections was not observed for heating temperatures above 300ºC, as shown in Figure 2 for the sample SP10C. Excess C present in martensite can be progressively released as carbide precipitates or transferred to the retained austenite as the heating temperature increases.

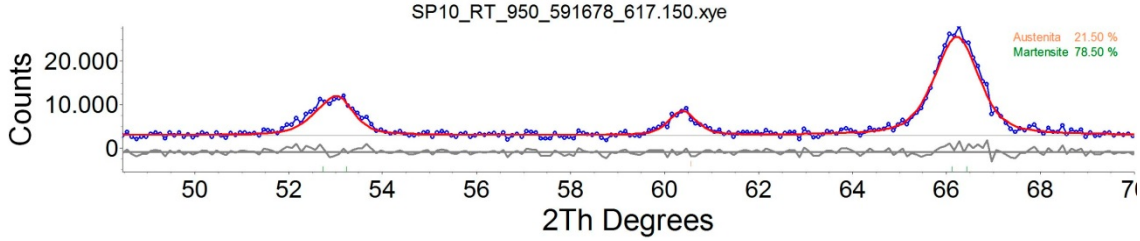

Figure 2 Results of Rietveld refinements of the NPD patterns recorded at 344ºC for the SP10C sample. The differences between experimental data (blue line) and the fitted simulated pattern (red line) are plotted as a continuous black line at the bottom.

c) Since anisotropic peak broadening of ferrite peaks in the samples with 0.4 and 0.5% would indicate that they correspond to tetragonal martensite, a structure with the space group I4/mmm was introduced for the structural model in the Rietveld refinement. However, the carbon content deduced from the c/a ratio is about 1.008. This value corresponds to an amount of C in solid solution

of about 0.2 mass%, which is much lower than the nominal one. This result would indicate that the volume fraction of autotempered martensite becomes dominant for carbon contents lower than 0.5 wt% and the Rietveld fitting would determine a c/a ratio of 1.008 as the average.

d) The austenite fraction remains constant at least up to approximately 400ºC in all samples, and the upper limit for the stability of austenite in each steel depends on the alloying elements present.

5. Conclusions and future work.

The development of new steel grades requires precise quantitative information on the phases present in the material and its evolution during the heat treatments to optimize their mechanical properties. Although XRD is the most used technique for this purpose, the penetration depth of Co radiation into Fe in laboratory X-ray diffractometers (about 30 μm) means that the volume contributing to diffraction may be too small to obtain a global average value of the microstructure. Microsegregation produced during solidification can cause the XRD patterns obtained in different samples of the same material to show very different values of the volume fraction of the phases present. In contrast neutron diffraction (ND) is particularly suitable to obtain the global averaged information due to a gauge volume of several mm^3.

We will carry out the following work with the NPD patterns obtained in the ILL:

a) Rietveld refinements of the NPD patterns of the initial martensitic microstructures will be performed including a structural model with austenite and two different martensite-like structures with different lattice parameters to account for both "fresh" and tempered martensite that form during cooling after the austenitization treatment.

b) The evolution of the phase fractions and tetragonality of these two colonies of martensite together with the fraction and lattice parameter of austenite will be determined during heating at 7.5ºC/min up to 950ºC by the Rietveld refinements of the NPD patterns. These results will be correlated with the dilatometric curves recorded at the same heating rate to delimit the temperature windows of the different tempering stages upon heating of martensitic microstructures and to provide systematic information on the microstructural changes that occur in each of these stages.

c) The evolution of microstructural parameters during heating will be compared with those obtained in samples heated to a given temperature at the same rate and then quenched to RT. It has been reported that the austenite lattice parameters both increases and decreases during tempering of martensitic microstructures, corresponding to the diffusion of C into untransformed austenite from supersaturated martensite (at temperatures lower than 400ºC) or carbide precipitation (at higher temperatures), respectively. A reduction in the C content of the austenite will produce an increase in the martensite start temperature that may destabilize this phase during cooling to RT. Therefore, the volume fraction of austenite determined at a given temperature in an in situ heating experiment by NPD will be compared with the value obtained by XRD in samples heated to this temperature and then quenched to RT to evaluate the austenite stability during the tempering treatment.

d) The crystallite size and lattice strain will determined simultaneously from line broadening of the NPD patterns following the double Voigt approach to evaluate when recovery and recrystallization take place in the microstructure.