AUSTENITE REVERSION DURING TEMPERING OF MARTENSITIC-FERRITIC STAINLESS STEEL

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Abstract

Martensitic-ferritic stainless steels (MFSS) have been developed by Vallourec for oil and gas application. Seamless tubes in this material are produced by quenching and tempering in order to assure yield strength higher than 110 ksi and better SSC resistance than supermartensitic stainless steels. During tempering, some amount of austenite can nucleate and grow inside the martensite. In the subsequent cooling, part of this austenite may transform into untempered martensite, while the other part remains as "reversed austenite". In order to improve the material and process design is essential to understand the microstructure evolution during the tempering process. In the present work, the austenite reversion was studied through in-situ high temperature XRD and the specimens were further characterized using SEM and TEM. Partitioning of elements during cooperative formation of austenite and Cr-rich phases ($M_{23}C_6$ carbides and Chiphase) were evidenced through EDX maps. The factors that control this partitioning process are discussed.

1. Introduction

Martensitic-ferritic stainless steels have been recently developed to produce tubings and casings for OCTG applications. Many oil fields present environments (pH_2S , pH and Cl^- content) aggressive enough for supermartensitic stainless steels (SMSS) and the selection of duplex metallurgy leads to significant increase on project costs. The corrosion performance of a SMSS have been improved in the past decades, basically in two ways: (1) by increasing slightly chemical composition and keeping the microstructure fully martensitic and (2) by increasing significantly chemical composition but producing, instead, a martensitic-ferritic microstructure [1-8]. The presence of delta ferrite in the martensitic-ferritic stainless steel (MFSS) is a natural consequence of the increasing on Cr and Mo contents, which is necessary to improve corrosion resistance. The MFSS alloy design keeps the martensite as the main microstructure, allowing reaching high mechanical properties by quenching and tempering.

The steel used in this work is a martensitic-ferritic stainless steel developed by Vallourec with 15% of Cr and higher Mo and lower Ni contents than a commercial SMSS. After a typical seamless tube rolling process this steel presents about 20% of δ ferrite and this amount is keep the same even after a quenching and tempering. A particular transformation shared by both

SMSS and MFSS is the austenite reversion in a range of temperatures typically found in tempering process. The understanding of this transformation is a key to develop and improve the processing necessary to guarantee mechanical properties and corrosion performance.

Many researchers have been studying the effect of chemical elements and processing parameters on retained austenite [9-12]. Nevertheless, the impact of reversion process on mechanical properties and corrosion behavior is not limited to the amount of retained austenite after a tempering cycle. The chemical variations promoted inside martensite by the reversion process play also a very important role on the MFSS performance. This paper presents the results of the study performed to better understand the austenite reversion kinetics by using *in situ XRD* measurements, thermodynamic simulation, SEM and TEM characterization.

2. Materials and Methods

The MFSS steel used in this work have the chemical composition presented in Table I. The Cr and Ni contents are higher than what could be find in any commercial SMSS and, as consequence, some delta ferrite will be expected in the final product. The steel was conventionally casted and rolled in 180 mm bars and then used to produce tubes with 133 x 22 mm (outside diameter x wall thickness) by continuous mandrel mill process. Those tubes were further industrially reaustenitized at 1000°C by 30 min and water quenched. The as quenched microstructure was composed by 22% of δ ferrite and 78% of martensite [8].

Table I. Chemical compositions of the steel used in the work (in wt%).

С	Si	Mn	Cr	Ni	Mo	Cu
0.012	0.23	0.32	14.4	4.7	3.3	0.86

Specimens for "in situ" X-ray diffraction (XRD) were taken from pieces of those as quenched tubes. Those specimens were cut longitudinally with 20 x 20 x 3 mm, in such a way that the square surface is perpendicular to the hoop direction. *In situ XRD* was performed in a Bruker D8 Discover diffractometer using Co K α radiation equipped with an Anton PaarTM GmbH chamber. Tempering simulations were carried out at temperatures ranging from 600 to 750°C with additional characterizations performed at room temperature, before and after each tempering simulation. For tempering simulations, the specimens were heated at 0.2°C/s until the specified temperature and soaked for 66 min, the necessary time to perform 6 measurements of 11 min in the window of 45 to 105° 20. After this period of time at tempering temperature, the specimens were cooled down to room temperature at 1.0°C/s. Rietveld Quantitative Analysis performed with Difrac Plus TOPAS 4.2 software was used to calculate the reversed austenite volume fraction.

Microstructures after *in situ XRD* simulations was characterized by SEM in a FEI Inspect S50 operating at 15 kV. Additional specimens for TEM investigation were produced from the as quenched tube. Longitudinal cylinders were machined from blanks tempered at selected temperatures and then cut in discs for thin foil preparation. Thin foils were prepared by a Struers TenuPol-5 twin-jet electropolishing, in a chemical solution of 9% perchloric acid and 91% ethanol at 23 V and -17°C. TEM investigations were performed in a FEI TitanTM G2 80-200, a FEG scanning transmission electron microscope (STEM) with ChemiSTEMTM technology, operating at 80 kV. EDX maps were performed in regions containing both ferrite and martensite to investigate the elements partitioning.

3. Results and Discussions

Diffractograms of XRD performed during the tempering cycle at 675°C are shown in the Figure 1, as an example. Additional diffractograms done at room temperature, before and after such tempering, are also shown. Before the tempering, the measured amount of retained austenite was very low, between 1.6 and 2.2% for all the specimens. During *in situ XRD* measurements, austenite reversion was evidenced by the increase in the peaks related to the (111), (200) and (220) planes with the tempering time. The volume fraction of reversed austenite as function of temperature and time is summarized in the Figure 2, together the maximum expected value from thermodynamic simulations through ThermoCalcTM. Those thermodynamic simulations considered only the chemical composition of austenite phase, in a microstructure presenting 22% of δ ferrite.



Figure 1. Difractograms performed before, during and after tempering cycle at 675°C.

After *in situ XRD*, each specimen was cooled down and the volume fraction of austenite retained at room temperature was determined and shown additionally in the Figure 2. It can be seen a peak of retained austenite after cooling from 675°C. At temperatures below this peak, the amount of reversed austenite was kept roughly the same after cooling down to room temperature. The slightly higher values observed after cooling from 650 and 675°C can be attributed to the fact that the peaks related to austenite plane (111) and ferrite plane (110) are determined at the beginning of measurement cycle. Above 675°C the reversed austenite will transform in to fresh martensite during cooling and just a small part will be kept retained at room temperature.

The microstructure after each tempering cycle was evaluated by SEM. Figure 3 shows images obtained by secondary electrons in the specimens tempered at 600, 650, 675 and 725°C. The retained austenite after reversion process can be easily identified in the specimens treated from 600 to 675°C (Figs. 3a, 3b and 3c). At 725°C, nevertheless, it is hard to point the retained austenite in the Figure 3d. After reversion of 52.5 vol %, only 5.8 vol % remained at room

temperature and this is less than the 7.4 vol% observed in the specimen tempered at 650°C, shown in Figure 3b. Then, the martensite area shown in Figure 3d is a rather a mixture of high temperature tempered martensite, fresh martensite formed during cooling and retained austenite.



Figure 2. Volume fraction of reversed austenite measured by using XRD data as a function of tempering temperature and soaking time together with the equilibrium state calculated by ThermoCalcTM.

TEM investigations were performed in the additional specimens from the same pipe, tempered in laboratory specifically for this purpose. Images obtained through TEM on high angle annular dark field (HAADF) mode and by hyper mapping of EDX signal are shown on Figures 4 and 5, respectively for specimens tempered at 600 and 675°C. Figure 4 shows the microstructure after tempering at 600°C with Cr and Mo rich δ ferrite grain (F) and Ni rich tempered martensite grain (M). Ni rich areas could be identified inside the tempered martensite as shown in the Ni EDX map of Figure 4b. Selected area diffraction (SAD) confirmed the FCC structure in such areas. Similar features can be seen on Figure 5, where higher quantity of reversed austenite could be identified inside tempered martensite. On this same specimen it was possible also to confirm the presence of Cr rich M₂₃C₆ carbides and Mo rich Chi-phase, both of them expected to be stable at this temperature, according to ThermoCalcTM simulations. Another important point is that those precipitates are located at vicinities of reverted areas, indicating substitutional elements diffusion in opposite direction: Cr and Mo towards precipitates and Ni towards reverted austenite.

The transformation kinetics can be described by the *Harper* and *Johnson-Mehl-Avrami* [13, 14] Equation 1:

$$\frac{\gamma_{(t)}}{\gamma_{\max}} = 1 - e^{\left[-(kt)^n\right]} \tag{1}$$

Where: $\gamma_{(t)}$ is the reversed austenite amount at the time *t*, γ_{max} is the maximum thermodynamically expected for a given temperature, *n* is and numeric exponent related to the nucleation mechanism and it is independent of temperature, *t* is the time at constant temperature and *k* is a temperature dependent parameter related to the nucleation and grow rates. This parameter is related to the apparent activation energy associated to the reversion process and can be given by the Equation 2:

$$k = k_0 \cdot e^{\left(\frac{-\Delta H}{RT}\right)}$$
⁽²⁾

Where: k_0 is a constant, ΔH is the apparent activation energy, R is the universal gas constant and T is the absolute temperature.

By operating properly the Eq. 1 and using the experimental data, both *n* and *k* can be obtained as for each tempering temperature. Finally, as plotted in Figure 6, using values of *k* and *T* in the Eq. 2, ΔH was found to have the value of 276.5 ± 24.3 kJ.mol⁻¹. This value is in the same order of magnitude of activation energy for diffusion of substitutional elements in iron. The activation energies associated to diffusion of Cr, Ni and Mo in the α -iron are, respectively, 229.9, 247.8 and 241.6 kJ.mol⁻¹ [15, 16, 17]. On the other hand, for diffusion in the γ -iron those activation energies are 218.6, 283.4 and 247.0 kJ.mol⁻¹, respectively [17, 18, 19]. The apparent activation energy found in this work indicates that the reversion process during tempering is associated with partition of substitutional elements between tempered martensite and the reversed austenite.



Figure 3. Microstructure observed at SEM in the specimens tempered at (a) 600°C, (b) 650°C, (c) 675°C and (d) 725°C.



Figure 4. Microstructure observed at TEM in the specimen tempered at 600°C presenting: (a) HAADF image, (b) Ni EDX map, (c) Cr EDX map and (d) Mo EDX map.



Figure 5. Microstructure observed at TEM in the specimen tempered at 675°C presenting: (a) HAADF image, (b) Ni EDX map, (c) Cr EDX map and (d) Mo EDX map.



Figure 6. Determination of apparent activation energy for reversion process.

4. Conclusions

The austenite reversion kinetics in a martensitic-ferritic stainless steel was studied by *in situ XRD* and the final microstructure was assessed by SEM and TEM. From this study it could be concluded that:

- At temperatures below 600°C the reversion process is negligible. From this temperature on, the austenite reversion increased continuously with both temperature and soaking time.
- After cooling from tempering cycle, different amounts of retained austenite, tempered martensite and fresh martensite could be observed, depending of tempering temperature. At temperatures below 675°C all the reverted austenite remains at room temperature after cooling. Nevertheless, above this temperature most of reverted austenite transforms in to fresh martensite and only a small part is retained at room temperature. At the peak temperature, a maximum of 23.6% of retained austenite was observed after cooling.
- The austenite reversion process depends on diffusion of substitutional elements. Ni diffuses toward austenite that is being formed while Cr and Mo diffuse in opposite direction, toward precipitates, mainly $M_{23}C_6$ and Chi-phase.
- The apparent activation energy for austenite reversion process was 276.5 kJ.mol⁻¹. This value is very close to the activation energy for diffusion of Cr, Ni and Mo in the iron matrix.

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