Effects of carbide-forming elements on the response to thermal treatment of the X45Cr13 martensitic stainless steel

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The effects of carbide-forming elements on the response to thermal treatment of the X45Cr13 martensitic stainless steel have been investigated. Heat treatments consisted of austenitizing for 60 s at temperatures ranging from 1000–1250 °C. The higher is the solution treatment temperature, the less M23C6 carbide is left out of solution in the austenite. As a result, the concentration of carbon and alloying elements in the martensite increases and, therefore, an increase in the hardness until a maximum value of 710 HV was found at austenitizing temperatures of 1120 and 1130 °C for the steels X45Cr13 and X45CrMoV14, respectively. At higher austenitizing temperatures, the presence of retained austenite was observed, which leads to a lowering of the hardness value. The higher amount of carbide-forming elements in the X45CrMoV14 determines an increase in retained austenite from 3 vol % to about 30 vol %. Thus, a drop in the hardness value from 710 to 680 and 585 for the steels X45Cr13 and X45CrMoV14, respectively, was found.

1. Introduction
Martensitic steels containing 12%–17% Cr, 0.1%–1.0%C are finding increasing application as high-strength corrosion-resisting structural steels in a wide range of applications, which include petrochemical and chemical plants, power plants, and gas turbine engines [1, 2]. These steels are fully austenitic at temperatures of 950–1000 °C and they become martensitic by air hardening even for large section sizes. In addition, a high chromium content develops a passive film in the alloy thus providing considerable corrosion resistance at temperatures up to 700 °C.

The design criteria for the 12%–17% Cr, 0.1%–1.0%C high-strength structural stainless steels includes the absence of delta ferrite at the austenitizing temperature, a martensitic transformation temperature above room temperature, and a maximum tempering resistance [3]. The most obvious strengthening mechanism in these steels is the martensitic reaction. For this reason, the heat treatment and chemical composition of the alloy must be adjusted to ensure a structure free of ferrite at the dissolution temperature and to avoid the retention of austenite upon cooling [2].

Because the steel must be tempered at as high temperature as possible to achieve the highest possible level of ductility, toughness and stress corrosion resistance, it is necessary to alloy it in order to increase the tempering resistance. The most effective alloying additions are the ferrite formers, such as molybdenum and vanadium [1, 2]. However, these elements tend to produce delta ferrite in the structure at the conventional austenitizing temperatures [4]. Therefore, it is necessary to balance the constitution by the addition of austenite-forming elements such as carbon, nickel, manganese or cobalt.

Any alloying element applied to improve the tempering resistance will further depress the martensitic transformation temperature and will increase the tendency for retained austenite to be produced. The effect of retained austenite depends on the percentage of these alloying elements. An amount of retained austenite higher than 10 vol % significantly reduces the yield strength and hardness. Another serious reaction is the later martensitic transformation following tempering. The change in volume associated to this transformation could lead to cracking. A double tempering is intended to temper any martensite formed this way.

The present work was carried out to investigate the effects of carbide-forming elements like chromium, molybdenum and vanadium on the response to thermal treatment of a martensitic stainless steel containing 13 mass % Cr and 0.45 mass % C. When alloying...
with such elements, in this steel an increase in the amount of the retained austenite is expected, but there was only a few systematic quantitative studies on that score so far. In this paper, the amount of the retained austenite determined by X-ray diffraction has been compared with the microstructure and hardness value in the steels X45CrMoV14 and X45Cr13 after austenitizing for 60 s at temperatures ranging from 1000–1250 °C.

2. Experimental procedure

Two steels have been prepared by arc melting in order to investigate the effects of the carbide-forming element on the response to thermal treatment of an X45Cr13 martensitic stainless steel. The detailed chemical compositions of the alloys are given in Table I. The steels are supplied in the spheroidized annealing form, the microstructure of which consists of globular M$_{23}$C$_{6}$ carbides distributed homogeneously in a ferrite matrix.

Heat-quenching treatments were performed in samples 12 mm long and 2 mm thick. These samples were heated at a constant rate of 0.5 °C s$^{-1}$ in a tungsten resistor furnace, equipped with ultrascemsive electronic programming, control and regulation systems. Radiation was focused on the samples, which were kept at an austenitization temperature ranging from 1000–1250 °C for 60 s and cooled down at a constant rate of 2 °C s$^{-1}$.

The as-received materials and those after heat treatment, were characterized using various techniques, including X-ray diffraction, optical microscopy (OM), and hardness measurements.

Identification of the phases present, lattice parameter measurements, and the amount of retained austenite were determined on the specimens by X-ray analysis [5, 6]. The diffraction studies were performed employing CuK$_{α}$ radiation. Automatic step scanning allowed the accumulation of a sufficient number of counts at each Bragg angle to obtain the desired statistical accuracy. The lattice parameter of austenite was calculated by the least-square method and these measurements were reproducible within 0.0001 nm. However, direct measurement of the tetragonality of the martensite was not possible, because lattice microstrains cause each pair of martensite lines to merge with its neighbour and an associated broad peak is observed. However, a comparison between the position of the martensite reflection and the value of the full-width at half-maximum (FWHM) of these peaks can give some idea about tetragonality of the different martensites. An increase in the tetragonality of the martensite causes a reduction on the angle 20 and a widening of the diffraction peaks.

In the austenite quantity calculations, attempts were made to consider the presence of texture in the microstructure. Thus, the $\alpha/\gamma$ volume ratio was calculated from the integrated intensities of the (1 1 1), (2 0 0), (2 2 0), (1 1 3), (2 2 2) and (4 0 0) austenite peaks, and the (1 1 0), (2 0 0), (1 1 2), (2 2 0) and (1 3 0) ferrite lines [7]. In the case of the material austenitized at temperatures above 1170 °C, at least five measurements on different samples were performed in order to improve the precision of the results in the coarse-grain-size microstructures. The final intensity of each peak was obtained by summation of the integrated intensities from the different diffraction patterns.

The microstructure was examined by OM. Metallographic preparation included mounting the samples in bakelite and polishing by the conventional method. The microstructure was revealed by chemical etching with Murakami’s reagent (100 g NaOH + 10 g K$_{3}$Fe(CN)$_{6}$ + 100 ml H$_{2}$O). This reagent causes preferential etching on carbides, allowing the quantification of carbide volume fraction by means of an automatic image analyser IBAS 2 from KONTROM. The image analyser was also used to measure the austenitic grain size after the austenitizing treatments.

Vickers hardness tests were carried out on samples of both tool steels after austenitizing at various temperatures. The results given correspond to the average of at least five tests.

3. Results

3.1. X-ray diffraction

The X-ray diffraction patterns of the X45CrMoV14 and X45Cr13 steels in the as-supplied form show only the presence of carbide M$_{23}$C$_{6}$. Fig. 1a and b show the X-ray diffraction patterns of the X45CrMoV14 and X45Cr13 steels, respectively. The intensity of the X-ray peaks corresponding to this carbide is quite similar in both steels, indicating a similar carbide volume fraction. The intensity of the carbide peaks decreases when the austenitizing temperature increases and after a treatment for 60 s at 1100 °C, these peaks disappear.

A progressive reduction in the angle 20 and a widening of the ferrite peaks with increasing austenitizing temperature, was observed. Fig. 2 shows the change in the position 20 and FWHM for the (3 1 0)$_{γ}$ X-ray diffraction line as a function of the austenitizing temperature. As observed in this figure, the peaks broaden and move to lower values of 20 upto 1135 and 1200 °C for the steels X45Cr13 and X45CrMoV14, respectively. The position and FWHM of the line profile remain constant at higher austenitizing temperatures. This effect was associated with an increase of the tetragonality of the martensite when the amount of the dissolved carbon increases.

| TABLE I Chemical composition (wt %) of the steels used in this investigation |
|-----------------|---|---|---|---|---|---|---|---|---|---|
| Steel           | C  | Si | Mn | P  | S  | Cr | Ni | Mo | V  |
| X45CrMoV14      | 0.46| 0.46| 0.44| 0.018| 0.003| 14.3| 0.16| 0.51| 0.13|
| X45Cr13         | 0.45| 0.32| 0.44| 0.030| 0.016| 13.0| 0.38| —  | —  |