JOURNAL OF MATERIALS SCIENCE **33** (1998) 4095–4100

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

C. GARCÍA DE ANDRÉS, L. F. ÁLVAREZ, V. LÓPEZ
Department of Physical Metallurgy, Centro Nacional de Investigaciones Metalúrgicas, C.S.I.C., Avda. Gregorio del Amo 8, 28040 Madrid, Spain

J. A. JIMÉNEZ
Department of Materials Technology, Max Planck Institut für Eisenforschung, Max Planck Strasse 1, D-40237 Düsseldorf, Germany
E-mail: jimenez@cenim.csic.es

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 $M_{23}C_6$ 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. © *1998 Kluwer Academic Publishers*

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 $0.5\,^{\circ}\mathrm{C\,s^{-1}}$ in a tungsten resistor furnace, equipped with ultrasensitive 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 $2\,^{\circ}\mathrm{C\,s^{-1}}$.

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 2θ 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 α/γ 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 $K_3Fe(CN)_6$ + 100 ml H_2O). 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 2θ and a widening of the ferrite peaks with increasing austenitizing temperature, was observed. Fig. 2 shows the change in the position 2θ and FWHM for the $(3\,1\,0)_\alpha$ 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 2θ 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	–	–

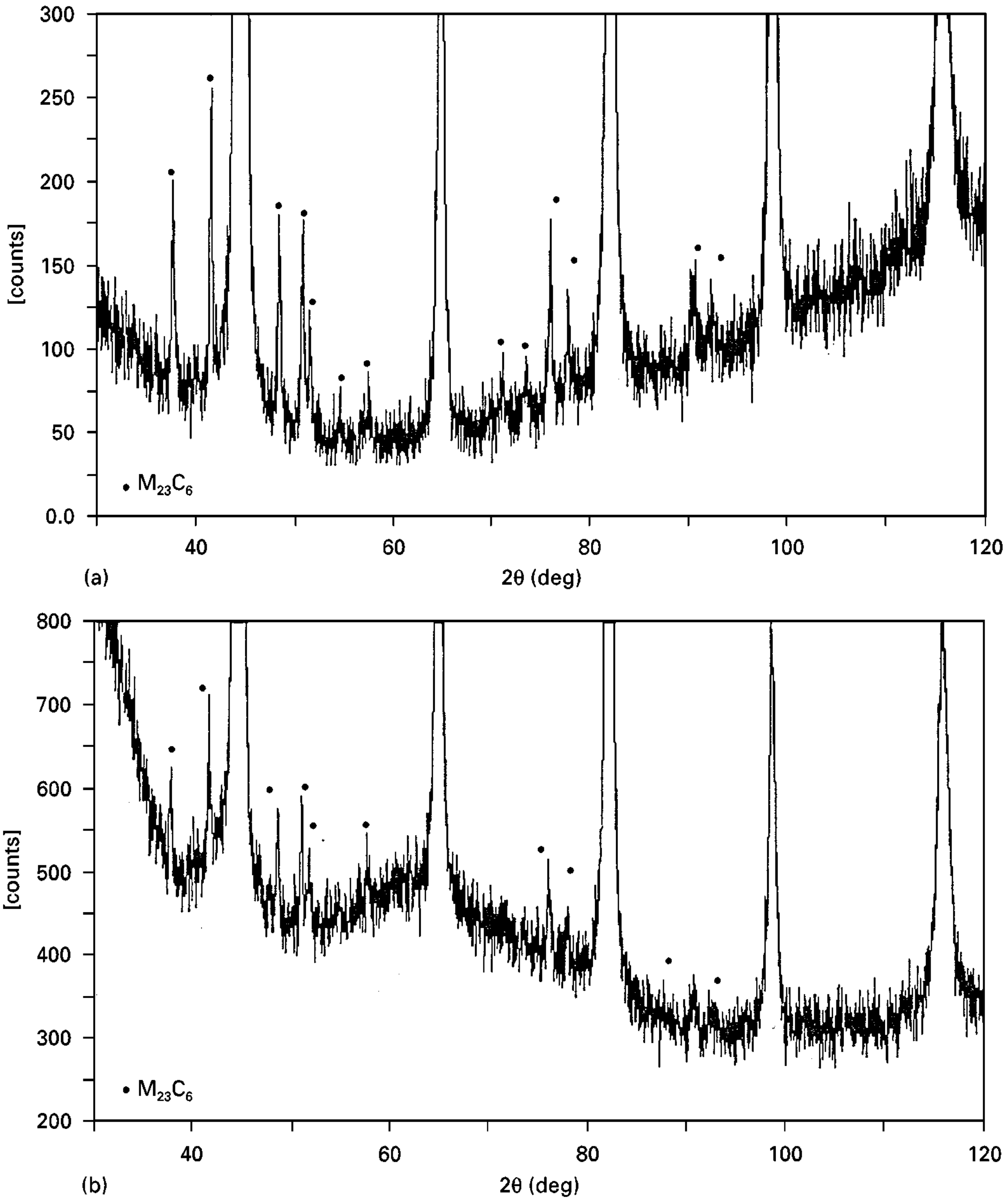

Figure 1 X-ray diffraction patterns of (a) X45CrMoV14, and (b) X45Cr13 steels in the supplied form.

The X-ray diffraction patterns of the X45CrMoV14 steel samples austenitized at temperatures above 1110 °C show the presence of retained austenite. The effect of the austenitizing temperatures on the volume fraction of retained austenite is presented in Fig. 3. By increasing the treatment temperature the amount of austenite increased upto a value of about 35 vol % at 1200 °C. This value remains constant for higher austenitizing temperatures. On the other hand, only a small amount of retained austenite was found in the X45Cr13 steel. A maximum value for the retained austenite volume fraction of about 3% was measured while austenitizing at temperatures ranging from 1135–1232 °C.

The lattice parameter of the austenite was determined only in the case of the X45CrMoV14, because the volume fraction of retained austenite in the X45Cr13 steel was too low to obtain a sufficient number of counts required for good statistical accuracy. A value of 0.3604 nm was obtained, which does not depend on the austenitizing temperature. This value for the lattice parameter and the empirical expression [8]

$$a = 0.3572 + 0.0033\%\,\mathrm{C} \qquad (1)$$

led to a carbon concentration of about 1% in the retained austenite.

3.2. Microstructure

In both steels, the microstructure in the spheroidized annealed form consists of randomly dispersed globular carbides $M_{23}C_6$ particles in a ferritic matrix, as shown in Fig. 4a and 4b. The carbide volume fraction is quite similar in both cases and a value of about 10 vol % was measured by image analysis.

The microstructures of the X45CrMoV14 steel after treatment at 1100, 1150, 1200 and 1250 °C are shown in Fig. 5. The structure is, in all cases, mainly martensite,

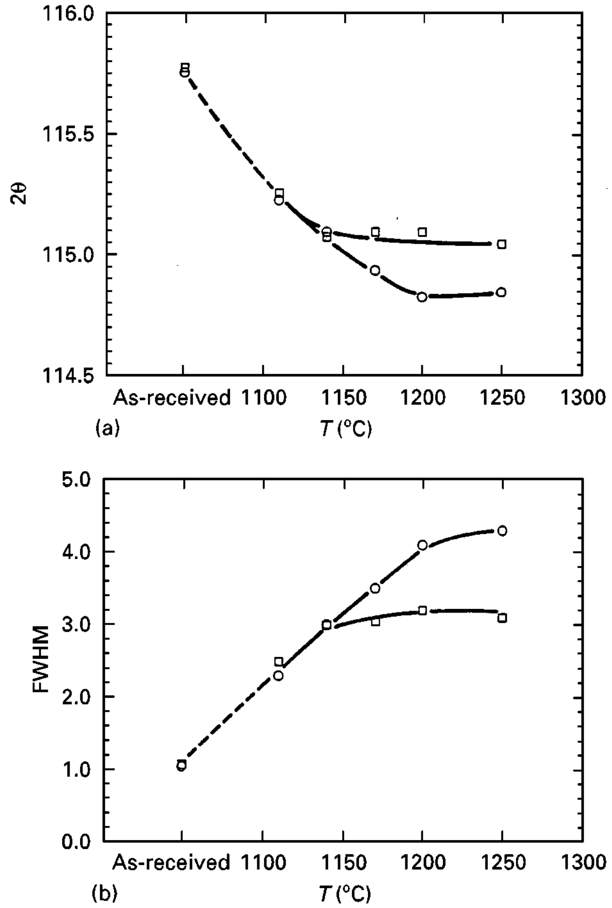

Figure 2 Effect of austenitizing temperature on (a) the position 2θ, and (b) FWHM for the $(3\,1\,0)_\alpha$ X-ray diffraction line. (○) X45CrMoV14, (□) X45Cr13.

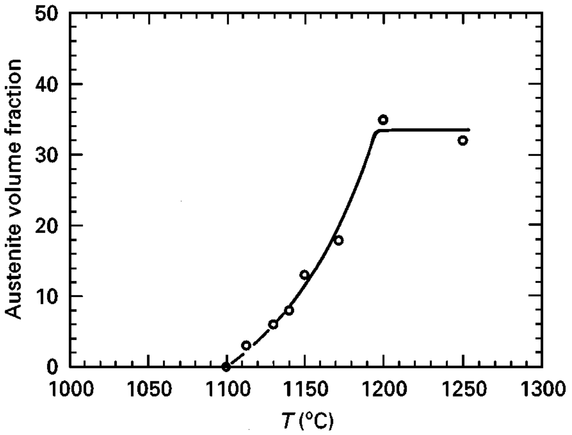

Figure 3 Retained austenite volume fraction as a function of the austenitizing temperature from X45CrMoV14 steel.

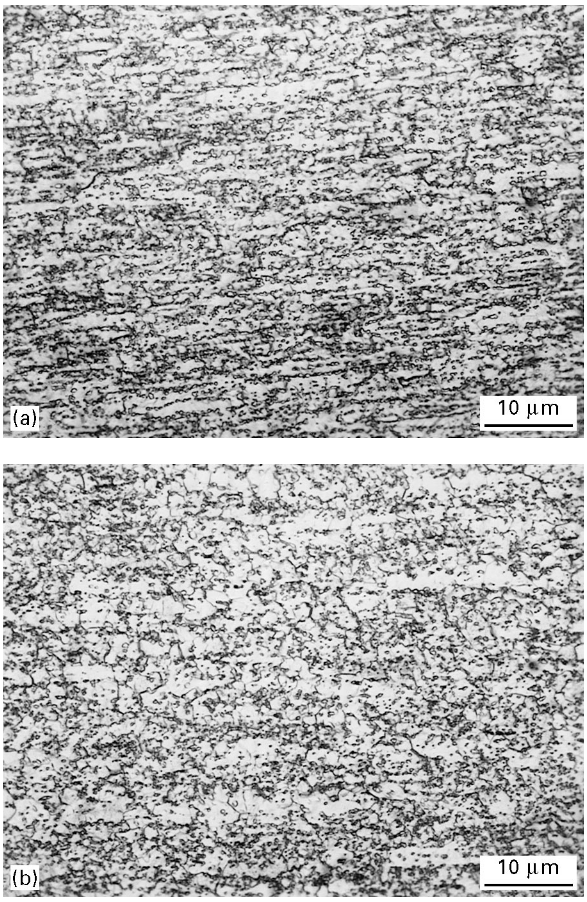

Figure 4 Optical micrograph of the (a) X45CrMoV14 and (b) X45Cr13 steels in the spheroidized annealed form. Etchant: Vilella's reagent.

but etching has revealed prior austenite grain boundaries. Although, according to X-ray diffraction patterns, retained austenite was present after austenitizing at temperatures above 1100 °C, no evidence of retained austenite was found by optical microscopy in samples austenitized up to 1150 °C (Fig. 5a and b). On the other hand, at austenitizing temperatures above 1150 °C (Fig. 5c and d) the structure consists of dark etched lath martensite and some white areas of retained austenite. However, direct measurement of the volume fraction of retained austenite was not possible as most of the laths and individual crystals of austenite are too fine for resolution in the light microscope.

The results of quantitative metallographic analysis after austenitizing at different temperatures are given in Figs 6 and 7. The grain-growth kinetics were quantified by the mean linear intercept grain size and the volume fraction of carbide was estimated by the area analysis method [9]. Severe grain growth is observed in Fig. 6 above 1120 °C, when the carbide volume fraction decreases to a value of about 1 vol %. The total carbide dissolution temperature is about 1130 and 1170 °C for the steels X45Cr13 and X45CrMoV14, respectively.

3.3. Hardness

The hardness values after an austenitizing treatment at various temperatures for 60 s are presented in Fig. 8. As shown in the figure, an increase of hardness was observed with increasing treatment temperatures up to a maximum value at 1120 and 1130 °C for the steels X45Cr13 and X45CrMoV14, respectively. This maximum value was about 710 HV5 in both cases. At higher treatment temperatures the value of hardness drops to a minimum value of 560 and 660 for the steels X45CrMoV14 and X45Cr13, respectively.

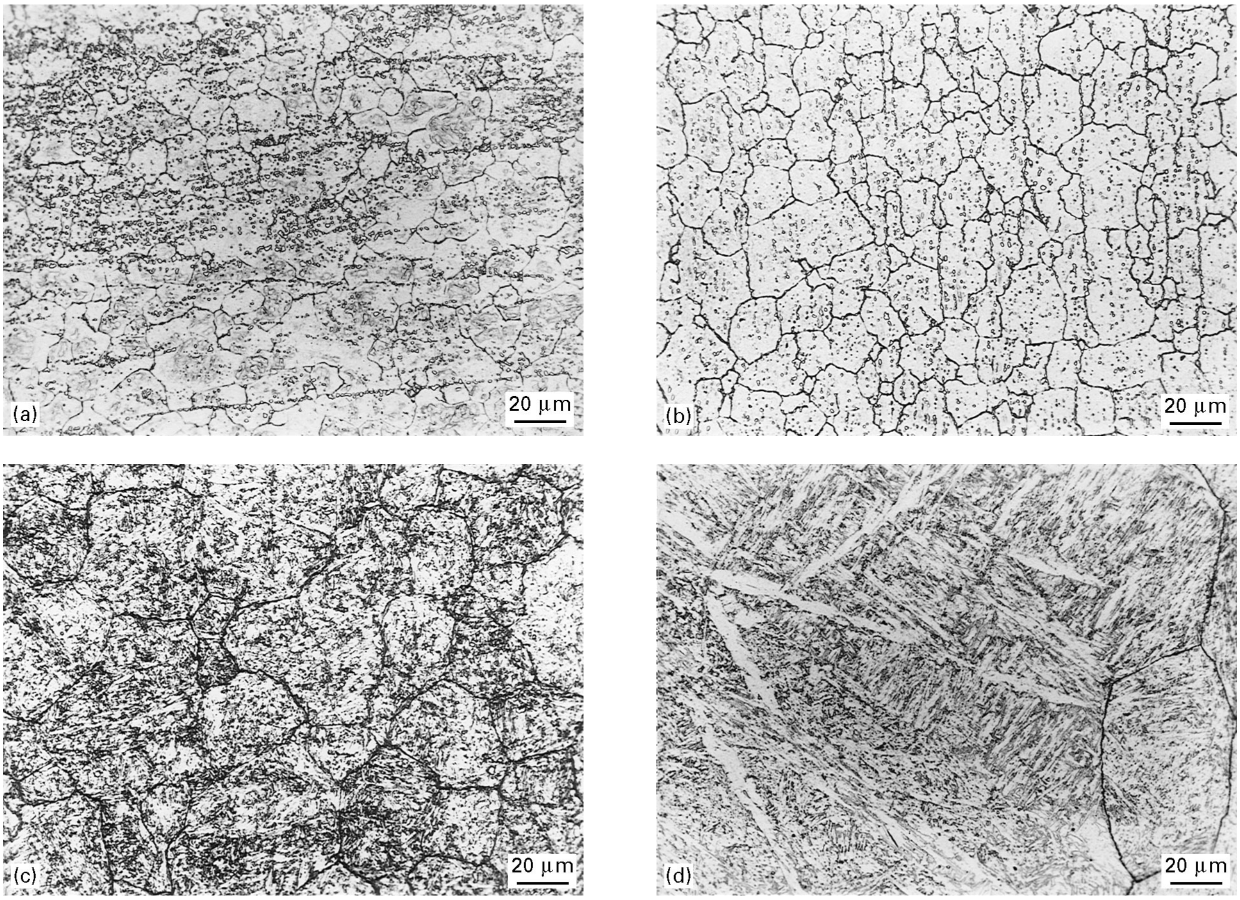

Figure 5 Microstructures of the X45CrMoV14 steel after a treatment at (a) 1100, (b) 1150, (c) 1200, and (d) 1250 °C for 60 s. Etchant: Vilella's reagent.

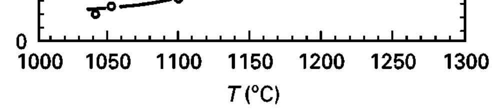

Figure 6 Effect of austenitizing temperature on the grain in the steels (○) X45CrMoV14 and (□) X45Cr13, respectively.

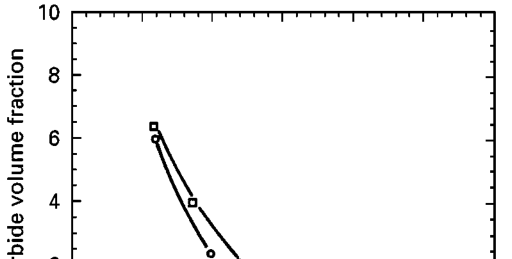

Figure 7 Effect of austenitizing temperature on the carbide volume fraction in the steels (□) X45CrMoV14 and (○) X45Cr13, respectively.

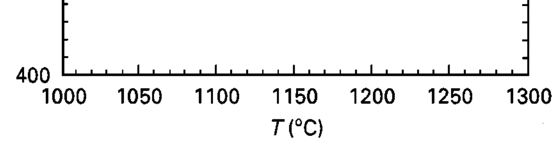

Figure 8 Vickers hardness after austenitizing treatment for 60 s at different temperatures: (○) X45Cr13, (□) X45Cr14MoV.

4. Discussion

X-ray diffraction analysis and microstructural observations performed on both steels in the as-received condition show that all carbon forms carbide $M_{23}C_6$. The amount of carbon is very similar in both steels and therefore a carbide volume fraction of about 10 vol % was measured in both cases.

The maximum hardness value for both steels is about 710 HV. This result clearly indicates that the addition of 0.51 Mo and 0.13 V has no solution-strengthening effect. The increase of hardness with the increase of austenitizing temperature must be associated with the martensite. For both steels, an increase in the austenitizing temperature causes a decrease in the carbide volume fraction. The amount of carbon dissolved in the austenite increases and then the tetragonality of the resulting martensite increases. This increase of tetragonality was confirmed by the progressive reduction of the angle 2θ and a widening of the ferrite peaks with the increase of austenitizing temperature. The position and FWHM of the line profile remain constant at austenitizing temperatures above 1135 and 1200°C for the steels X45Cr13 and X45CrMoV14, respectively.

Dissolution of $M_{23}C_6$ carbide causes an enrichment of carbide-forming elements and carbon content in the austenite, which therefore has a lower M_s temperature. Excessive enrichment of the matrix with an element capable of diminishing the M_s–M_f range determines the presence of residual austenite in the microstructure. This leads to a hardness peak at 1120 and 1130 °C for the steels X45Cr13 and X45CrMoV14, respectively. The volume fraction of carbide is lower than 1 vol % in both cases after austenitizing at these temperatures. At higher austenitizing temperatures, the presence of retained austenite, which is much softer than martensite, causes a decrease in the hardness value. A higher amount of carbide-forming elements in the X45CrMoV14 may determine a slower diffusion in the steel, because a higher temperature is required for dissolution of carbide. As a consequence, these elements retard diffusion-controlled transformation and cause a higher tendency for retaining the austenitic structure. So critical may be the effect of composition on the martensitic transformation temperature, that in the present work it was found that the maximum amount of retained austenite varied from 3 vol % to about 30 vol % for the steels X45Cr13 and X45CrMoV14, respectively. Thus, a drop in the hardness value from the maximum value of about 710 in both steels to 680 and 585, respectively, was found.

The maximum hardness values were obtained after a treatment at 1135 and 1200 °C for the steels X45Cr13 and X45CrMoV14, respectively. These temperatures lay in the homogenous austenite region, i.e. in this region, the hardness and the M_s temperature are independent of the austenitization conditions, because neither the carbon concentration nor the distribution of the alloying elements change within the usual austenitization times. Thus, a plateau is found in Figs 2, 3, and 8 for temperatures included in this region.

The grain growth that takes place at temperatures above 1120 °C can be explained on the basis of the reduced number of carbide particles present. In fact, the volume fraction of carbides was 2.5 vol % and lower than 0.5 vol % at 1100 and 1150 °C, respectively. Austenitizing of both steels at 1200 °C causes the total dissolution of carbide particles and then a strong coalescence of austenite grains is observed.

5. Conclusions

1. The increase in hardness of steels X45CrMoV14 and X45Cr13 with increasing austenitizing temperature is associated with an increase in the tetragonality of martensite when the amount of carbon dissolved increases. A maximum value of 710 HV was found for both steels.
2. The presence of residual austenite in the microstructure leads to the lowering of the hardness value and a maximum is observed at 1120 and 1130 °C for the steels X45Cr13 and X45CrMoV14, respectively.
3. A higher amount of carbide-forming elements in X45CrMoV14 determines an increase of 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.

Acknowledgement

The authors gratefully acknowledge the support of the Comisión Interministerial de Ciencia y Tecnología (CICYT) under Grant no. MAT. 93-1363-E.

References

1. F. B. PICKERING, *Int. Metals Rev*, **21** (1976) 1.
2. K. J. IRVINE, D. J. CROWE and F. B. PICKERING, *J. Iron. Steel Inst.* **195** (1960) 386.
3. K. J. IRVINE, D. T. LLEWELLYN and F. B. PICKERING, *ibid.* **192** (1959) 218.
4. W. STEVEN and A. G. HAYNES, *ibid.* **183** (1956) 349.
5. B. L. AVERBACH and M. COHEN, *Trans. AIME* **176** (1948) 401.
6. R. L. MILLER, *Trans. ASM* **57** (1964) 892.
7. U. WOLFSTIEG, *Härterei-Tech. Mitt.* **27** (1972) 245.
8. R. C. RULL and M. COHEN, *Trans. AIME* **245** (1969) 241.
9. F. N. RHINES, *Rev. Metal.* **22**(1) (1986) 3.

Received 3 November 1997
and accepted 15 May 1998