

PRECIPITATION OF $M_{23}C_6$ CARBIDES: THERMOELECTRIC POWER MEASUREMENTS

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Abstract.- The volume fraction of $M_{23}C_6$ carbides precipitated during cooling in an X45Cr13 stainless steel has been estimated from the thermoelectric power (TEP) measurement. Likewise, the different contributions to the TEP measurement of samples cooled at different cooling rates have been determined.

INTRODUCTION

Martensitic steels containing 12%-17%Cr, 0.1%-1%C are used 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. These steels are commonly used in quenched and tempered conditions [1,2]. The quenching microstructure of these steels always consists of martensite and complex carbides. There may also be some retained austenite present in the microstructure since carbon and chromium lower the martensite transformation temperature retaining austenite at room temperature.

In martensitic stainless steels, as in other alloyed steels containing carbide-forming elements, the presence of carbides in the quenched microstructure has a decisive effect on their properties [3]. Carbide control by means of the thermal parameters is vital to optimize the as-quenched properties of these steels. In this sense, the use of TEP measurement is helpful in the study of the precipitation process of carbides. In fact, this technique is very sensitive to the amount of atoms in solid solution in iron [4-8].

The influence of carbon and chromium contents in solid solution in the austenite, and the microstructure on TEP during the dissolution of $M_{23}C_6$ carbides were determined elsewhere [9]. It was found that TEP variations in the X45Cr13 stainless steel are mainly related to the increase in solid solution content of carbon. The effect of chromium on the TEP was found less significant than that of carbon. Likewise, the presence of retained austenite to the detriment of martensite in the microstructure increases the TEP. This behavior is related to the decrease in strain of the microstructure that occurs when the volume fraction of martensite is reduced. Based on those previous results, in this work the volume fraction of carbides precipitated is estimated from the TEP measurement of samples cooled at different cooling rates.

EXPERIMENTAL PROCEDURE

The chemical composition of the studied steel in mass-% is as follows: 0.45 %C, 13.0 %Cr, 0.38 %Ni, 0.32 %Si, 0.44 %Mn, 0.03 %P, and 0.016 %S. The material was obtained from a cold-rolled coil and was tested in annealed condition. As-received microstructure of this steel consists of

globular carbides finely distributed in a ferrite matrix (Figure 1). Thermodynamic equilibrium calculations and x-ray diffraction patterns showed elsewhere, demonstrated only the presence of $M_{23}C_6$ carbides in the as-received and as-quenched microstructures [10,11].

The precipitation process of $M_{23}C_6$ carbides has been investigated by the TEP measurement on samples, 30 mm in length, 2 mm in width and 0.8 mm in thickness, austenitized at 1120 °C at a heating rate of 0.5 °C/s. This temperature, named *optimum* temperature elsewhere [12], is the temperature at which the maximum quenching hardness is reached in this steel. At this temperature, only about 3 % of carbides remains undissolved. After 180 seconds of holding time, specimens were cooled at different cooling rates (0.5, 1, 2, 5, 10, 20 and 40 °C/s). These heat treatments correspond to cooling rates faster than the critical cooling rate at which austenite solely transforms to martensite (0.4 °C/s) in this steel.

The volume fraction of carbides present in the microstructure was estimated by a systematic manual point counting procedure on optical micrographs. Test pieces etched with Murakami's reagent were used for these measurements. Figure 2 shows optical micrographs of the as received and heat treated microstructures of the studied steel etched with this reagent. Carbides are coarse enough to be revealed by optical microscopy (~ 0.7 μm in diameter). Scanning electron microscopy also revealed the presence of much finer carbides precipitated on grain boundaries during cooling at rates lower than 20 °C/s (Figure 3), but their volume fraction was found negligible (less than 0.25 %).

Quantitative X-ray analysis was used to determine the volume fraction of retained austenite present in the heat treated microstructure. After grinding and final polishing using 0.25 μm diamond paste, the samples were etched to obtain an undeformed surface. They were then step-scanned in a Siemens D5000 X-ray diffractometer using unfiltered Cu K_α radiation. The 2θ scan rate was 0.03 degree min^{-1} . The machine was operated at 40 kV and 30 mA. The retained austenite content was calculated from the integrated intensities of (200), (220) and (311) austenite peaks, and those of (002), (112) and (022) planes of ferrite [13]. Using three peaks from each phase avoids biasing the results due to any crystallographic texture in the samples [14].

Vickers hardness tests were carried out on heat treated samples cooled at the above mentioned cooling rates. The results correspond to the average of at least five tests. The experimental procedure of the TEP measurement is described in detail elsewhere [9].

RESULTS AND DISCUSSION

The TEP value corresponding to the austenitization temperature of 1120 °C and the highest cooling rate tested (40 °C/s), equal to $S_{ref} = 4.189 \mu\text{V/K}$, was selected as the reference level for the study of carbide precipitation as a function of cooling rate in the steel. At this heat treatment condition, the majority of carbides have been dissolved during heating, the carbon and chromium of the steel is in solid solution in the austenite, and carbide precipitation is avoided during cooling. The TEP measurements were performed on samples with a martensite plus retained austenite microstructure. As a first approximation, contributions to the TEP due to magnetic, morphological differences, etc. in the microstructure are considered negligible.

Figure 4.a shows changes in the TEP of reference specimens ($\Delta S = S - S_{ref}$, being S the TEP value of a given sample) due to cooling rate in the studied steel. The curve shows an increase in the TEP as the cooling rate decreases. The observed TEP variations are related to the precipitation of carbides during cooling. Fig. 4.b shows the amount of carbides precipitated at the different cooling rates measured on micrographs such as those presented in Fig. 2. As expected, the lower the cooling rate, the higher the volume fraction of carbides precipitated. According to experimental results, precipitation of carbides is observed for cooling rates lower than 20 °C/s.

Figure 4.c shows the volume fraction of retained austenite present in the microstructure as a function of quenching cooling rate, together with the corresponding hardness evolution. By decreasing the cooling rate, the precipitation process of carbides is enhanced, reducing the

chromium and carbon contents in the austenite, and thus the amount of austenite retained in the microstructure. The increase in carbide volume fraction and the decrease in retained austenite content in the microstructure explain the increase in hardness observed as the cooling rate is slowed down.

Results in Fig. 4 suggest that any variation between the TEP value of the reference level and the TEP value at any other cooling condition shows quantitative differences in the volume fractions of carbides and retained austenite in the microstructure.

Authors determined previously [9] the contribution due to the difference in retained austenite volume fraction that affects the TEP measurement:

$$\Delta S_{microstr} = K_{microstr} \cdot (\Delta\% \gamma_{ret}) \quad (1)$$

where $\Delta S_{microstr}$ is the variation in the TEP due to the difference in retained austenite volume fraction in the martensite plus retained austenite microstructure, $K_{microstr}=0.087 \mu\text{V/K}\%$ and $\Delta\% \gamma_{ret}$ is the change in retained austenite volume fraction. Figure 5 represents the influence of microstructure on the TEP measurement in the stainless steel as a function of the variation in retained austenite volume fraction in the microstructure. The presence of retained austenite to the detriment of martensite in the microstructure increases the TEP. This behavior is explained by the decrease in strain of the microstructure that occurs when the volume fraction of martensite is reduced. It is well known that the reduction of dislocations leads to a positive TEP variation [15]. Once the influence of microstructure on the TEP measurement has been identified, it is possible to evaluate the contribution due to the carbon and chromium contents in solid solution in the austenite:

$$\Delta S_{C+Cr}^{SS} = \Delta S - \Delta S_{microstr} \quad (2)$$

where ΔS_{C+Cr}^{SS} is the contribution to the TEP due to the carbon and chromium contents in solid solution in the austenite; ΔS is the change in the TEP represented in Fig. 4.a; and $\Delta S_{microstr}$ is the variation in the TEP due to the difference in retained austenite volume fraction in the microstructure calculated according to Eq. (1). Figure 6 shows the influence of carbon and chromium contents in solid solution in the austenite and the influence of microstructure on the TEP measurements for the stainless steel. As expected, the contribution to the TEP measurement due to the carbon and chromium contents in solid solution increases as the cooling rate decreases. This figure also suggests that the increase in TEP measurement in the studied steel is mainly related to the decrease in solid solution content of carbon and chromium.

On the other hand, the following functions allows to estimate the individual contributions to the TEP due to the carbon and chromium content in solid solution in the austenite [9]:

$$\Delta S_C^{SS} = K_C \cdot [C]_{SS} = K_C \cdot [C]_{M_{23}C_6} \cdot \frac{[M_{23}C_6]_{precipitated}}{100} \quad (3)$$

$$\Delta S_{Cr}^{SS} = K_{Cr} \cdot [Cr]_{SS} = K_{Cr} \cdot [Cr]_{M_{23}C_6} \cdot \frac{[M_{23}C_6]_{precipitated}}{100} \quad (4)$$

where $K_C = 20 \mu\text{V/K}(\text{mass}\%)$ and $K_{Cr} = 0.30 \mu\text{V/K}(\text{mass}\%)$; $[C]_{SS}$ and $[Cr]_{SS}$ are the decrease in carbon and chromium in solid solution in mass-%, respectively, due to precipitation; $[C]_{M_{23}C_6}$ and $[Cr]_{M_{23}C_6}$ are the amount of carbon and chromium in $M_{23}C_6$ carbides, respectively; and $[M_{23}C_6]_{precipitated}$ is the volume fraction of carbides precipitated during cooling in percentage. According to thermodynamic calculations [16], the amount of carbon $[C]_{M_{23}C_6}$ and chromium

$[Cr]_{M_{23}C_6}$ in $M_{23}C_6$ carbides in the studied steel are about 5 mass-% and 55 mass-%, respectively, at all the temperatures tested, therefore the volume fraction of carbides precipitated during cooling, $[M_{23}C_6]_{precipitated}$, can be estimated as follows,

$$[M_{23}C_6]_{precipitated} = \frac{\Delta S_{C+Cr}^{SS} \cdot 100}{K_C [C]_{M_{23}C_6} + K_{Cr} [Cr]_{M_{23}C_6}} \quad (5)$$

In Fig. 7 the experimental and calculated volume fraction of carbide precipitated during cooling are compared. Points lying on the line of unit slope show perfect agreement between experimental and calculated values. The accuracy of the calculations is quantified by its square correlation factor, R^2 . The TEP values estimated from the equations proposed in this work are in good agreement (with an accuracy of 99 % in R^2) with the corresponding experimental results. It is remarkable how very small amount of carbides precipitated during cooling affect the TEP measurement. In this sense, this technique is a powerful method to study the dissolution and precipitation processes of carbides in stainless steels, specially when a small amount of carbides dissolves or precipitates during heat treatment.

Conclusions

In this work the different contributions to the TEP measurement during the precipitation process of $M_{23}C_6$ carbides in an X45Cr13 stainless steel have been evaluated. Thus, the influence of carbon and chromium contents in solid solution in the austenite and the microstructure on the TEP has been determined. Moreover, it has been shown that the volume fraction of carbides precipitated during cooling can be estimated from the TEP measurement with a good accuracy.

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Figure Captions

Figure 1.- a) Optical and b) scanning electron micrographs of the steel in as-received condition. Etched with Vilella's reagent.

Figure 2.- Optical micrographs of the steel: a) in as-received condition; after austenitization at 1120 °C and cooling at b) 40 °C/s, c) 20 °C/s, d) 10 °C/s, e) 5 °C/s, f) 2 °C/s, g) 1 °C/s and h) 0.5 °C/s. Etched with Murakami's reagent.

Figure 3.- Scanning electron micrograph of the steel after austenitization at 1120 °C and cooling at 20 °C/s.

Figure 4.- Results on samples austenitized at 1120 °C and cooled at different cooling rates; a) TEP measurements; b) volume fraction of carbides; and c) volume fraction of retained austenite present in the microstructure and corresponding hardness values.

Figure 5.- Influence of microstructure on the TEP measurement in the studied steel as a function of the variation in retained austenite volume fraction in the microstructure.

Figure 6.- Contributions to the TEP measurement during the precipitation process of $M_{23}C_6$ carbides in the X45Cr13 stainless steel.

Figure 7.- Comparison of experimental and calculated volume fraction of carbides precipitated during cooling at the different rates tested in the stainless steel.

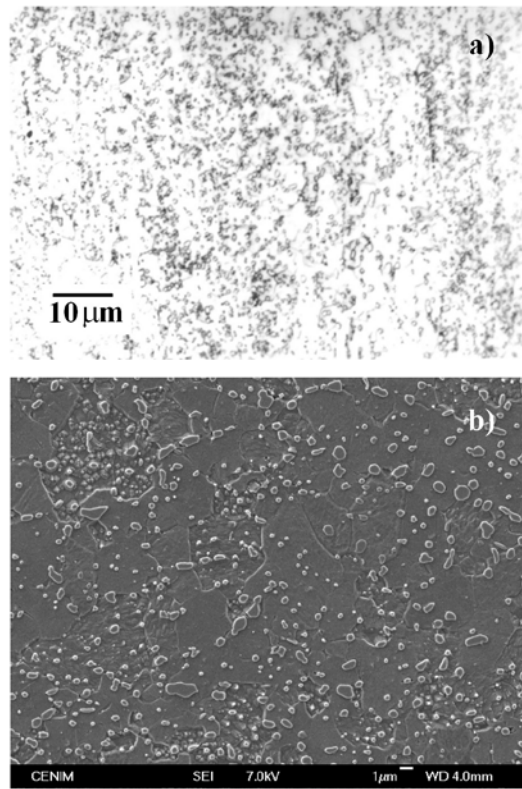


Figure 1

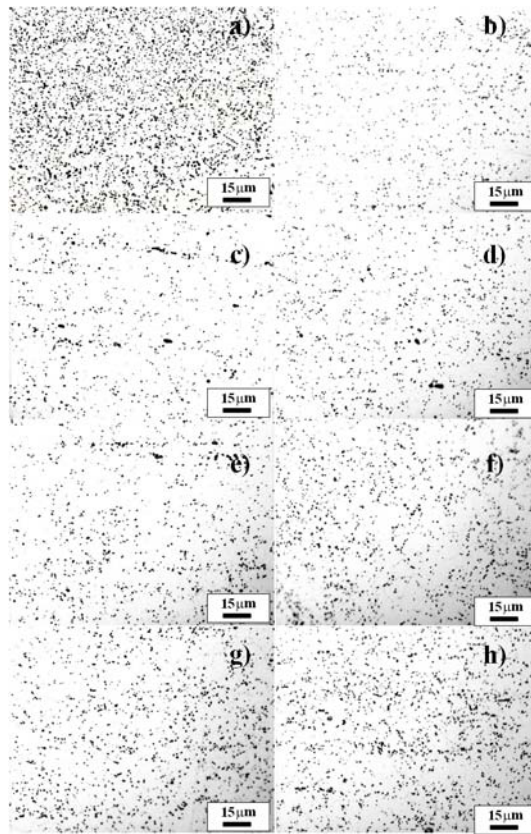


Figure 2

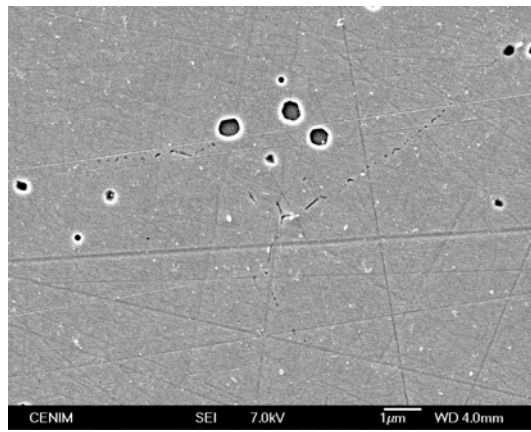


Figure 3

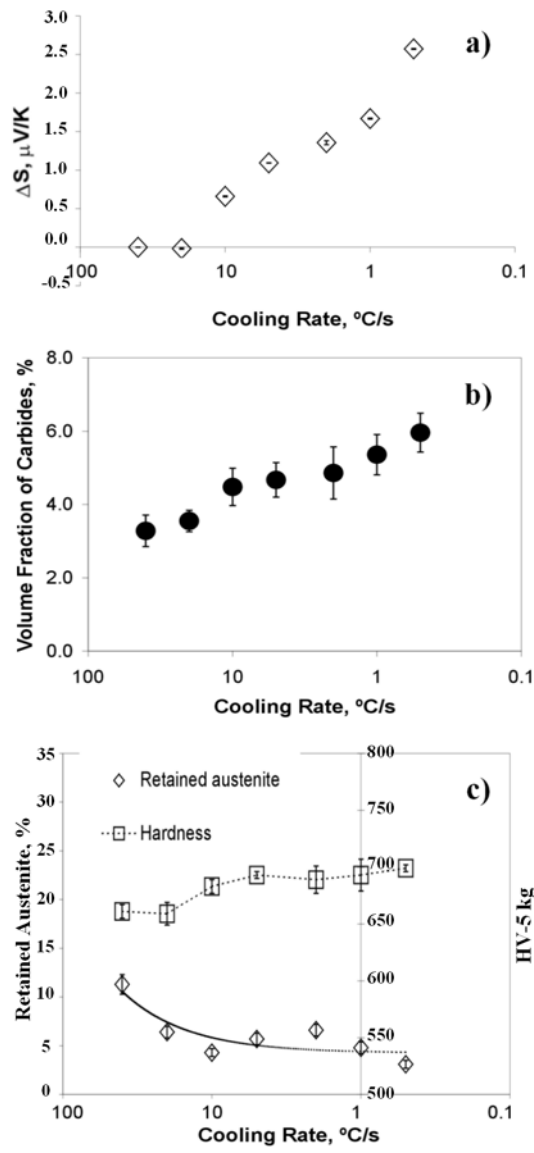


Figure 4

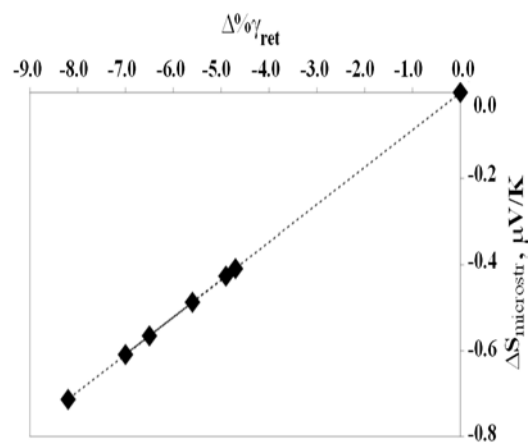


Figure 5

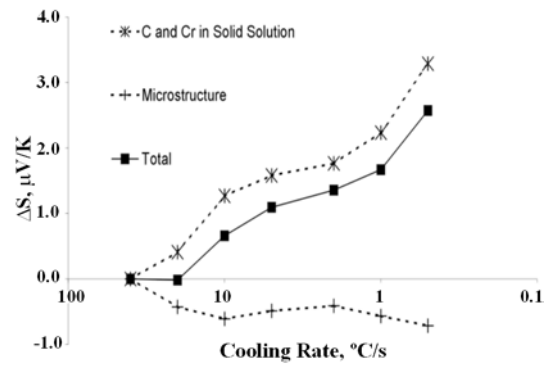


Figure 6

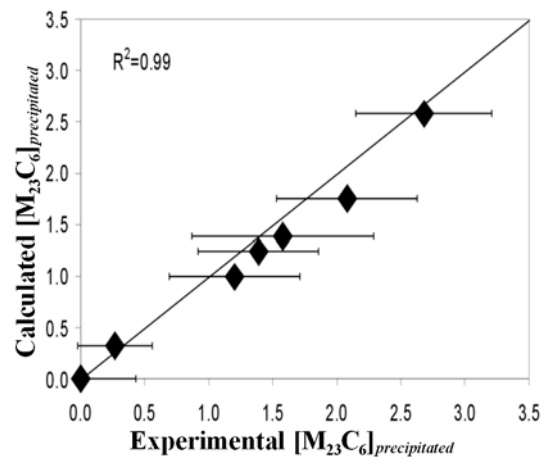


Figure 7