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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.

Keywords: Stainless steels; Carbides; Thermoelectric power

1. 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 forms [1,2]. The quenched 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 thus 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 influence of 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 to be 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.

2. Experimental procedure

The chemical composition of the studied steel in mass% is as follows: 0.45%C, 13.0%Cr, 0.38%Ni,

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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 (Fig. 1). Thermodynamic equilibrium calculations and X-ray diffraction patterns shown 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 carbide remains undissolved. After 180 s 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. Fig. 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 (Fig. 3), but their volume fraction was found to be negligible (less than 0.25%).

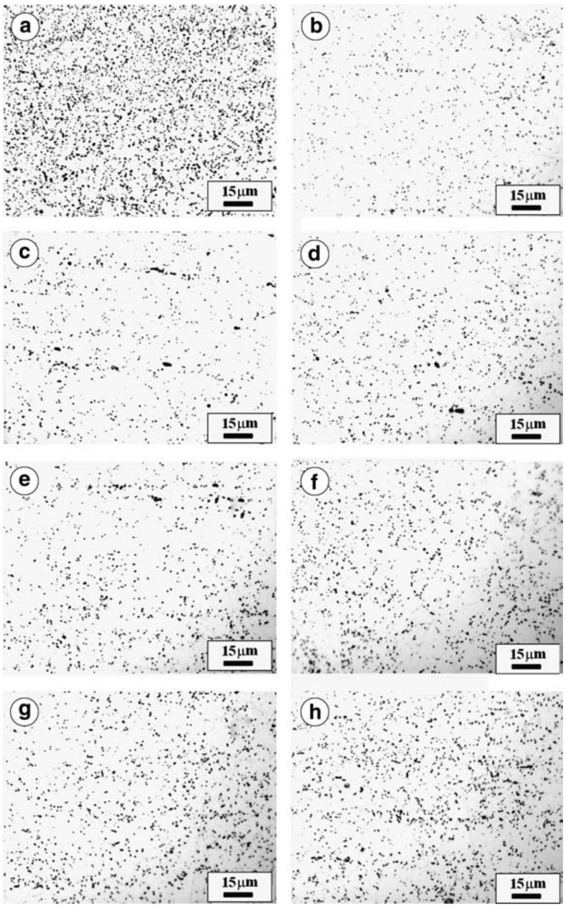

Fig. 2. Optical micrographs of the steel: (a) in as-received condition; after austenitization at 1120 °C and cooling at (b) 40 °C/s, (c) 20 °C/s, (d) 10 °C/s, (e) 5 °C/s, (f) 2 °C/s, (g) 1 °C/s and (h) 0.5 °C/s. Etched with Murakami's reagent.

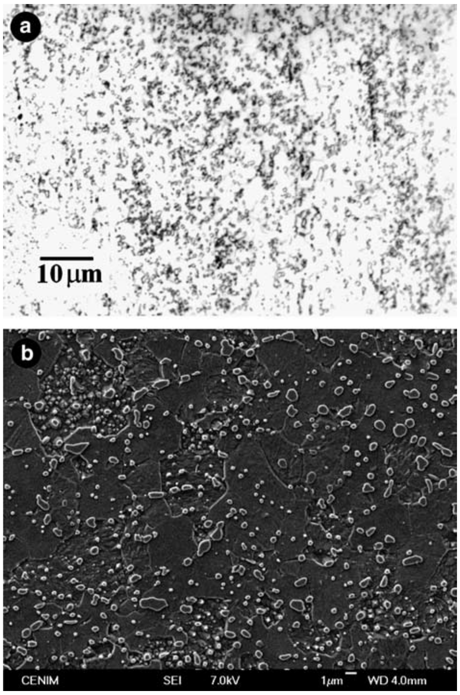

Fig. 1. (a) Optical and (b) scanning electron micrographs of the steel in as-received condition. Etched with Vilella's reagent.

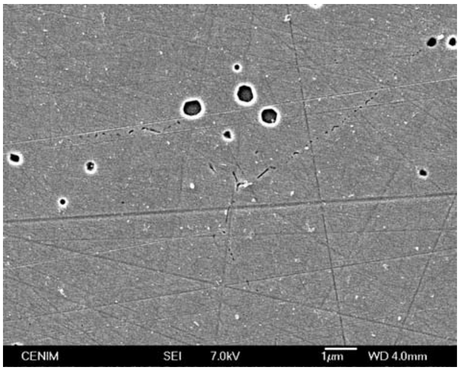

Fig. 3. Scanning electron micrograph of the steel after austenitization at 1120 °C and cooling at 20 °C/s.