NbC precipitates EELS spectra in a very low carbon microalloyed steel[(•)]

J.E. Mancilla* and C.A. Hernández*

Abstract   In this paper a characterization study by transmission electron microscopy (TEM) and electron energy loss spectroscopy (EELS) of NbC precipitates in microalloyed steel is presented. The steel was hot rolled in a laboratory scale two-high reversing mill. The shape, size, location, and number of particles per unit area in the steel microstructure are reported. The particles were semi quantitatively analyzed for the heavier alloying elements using EDS, while EELS was used for the lighter elements, e. g. carbon and nitrogen. The EELS study of the precipitates reveals that the carbon is present as a compound (NbC) without nitrogen.

Keywords   TEM. EELS. Microalloyed Steels. NbC Precipitates.

Espectros por EPEE de precipitados de NbC en un acero microaleado de muy bajo contenido de carbono

Resumen   En este trabajo se presenta un estudio de caracterización por espectroscopia de pérdida de energía de electrones (EPEE) realizado en un microscopio electrónico de transmisión de los precipitados de NbC en un acero microaleado. El acero se laminó en caliente en un laminador dúo reversible escala laboratorio. Las partículas de precipitados se caracterizaron en tamaños, formas y distribución y se analizaron semicuantitativamente para los elementos de aleación del acero más pesados, empleando un detector por dispersión de energías de rayos X, mientras que la EPEE se empleó para los elementos más ligeros, es decir, el carbono y el nitrógeno. El estudio por EPEE de los precipitados muestra que el carbono está presente como un compuesto (NbC) sin que se haya encontrado nitrógeno en los mismos.

Palabras clave   Microscopía electrónica de transmisión. Espectrometría de pérdida de energía de los electrones. Aceros microaleados. Precipitados de NbC.

1. INTRODUCTION

Small additions of niobium (< 0.1 wt. pct.) to low alloy steels are used to increase the mechanical properties by grain refinement and precipitation hardening[1 and 2]. The role of niobium in a micro-alloyed steel is related to its capability to strengthen steels, more than vanadium and titanium, mainly by precipitation and solid solution. The former will imply that carbides and carbo-nitrides of Nb will precipitate during deformation at high temperatures (strain induced precipitation) and by coherent precipitation during transformation to ferrite. Another primary effect of these precipitates is a grain refinement.

It is also known that niobium in solid solution is the most effective element to delay static recrystallization, in comparison to titanium and vanadium[3 and 4].

The precipitation kinetic is a function of the process variables and chemical composition[5]. For a better understanding of the precipitation kinetic it is important to describe quantitatively the particles in terms of chemical composition, size, shape and distribution of the precipitates[6]. The Transmission Electron Microscope (TEM) is the technique used to differentiate between different forms and sizes (< 200 nm) present in Nb-microalloyed steel. TEM morphological studies of microalloyed steel precipitates demonstrated the complexity of the precipitates[7-9]. In the as-cast condition it has been found that very complex precipitates were formed. With various thermomechanical treatments it has been found

that the Nb:C stoichiometric ratio of deformation-induced precipitates is about 1:1, cubic shape and about 10–150 nm in size[10].

Recent developments in microscopy techniques (EFTEM, EELS, APFIM, and ELNES) have been applied to the study of microalloyed steels precipitates[11 and 12]. Electron energy-loss spectrometry (EELS) is a powerful analytical technique to study precipitates in steels. The characteristic peaks for zero-loss electrons and plasmon interactions are followed by the core-loss adsorption edges. Although there is great amount of articles and congresses that report the morphological characteristics of the precipitates, it is important to know the EELS spectrum of NbC precipitates of steels[13]. In this work, a morphological TEM characterization and an electron energy loss spectroscopy study of NbC precipitates and surrounding steel matrix in a very-low carbon niobium microalloyed steel is presented.

2. MATERIALS AND METHODS

The niobium microalloyed steel composition used in this study is given in table I. 250 kg metal charge was melted in an electric induction furnace. The metal charge consisted of electrolytic iron, very low carbon steel scrap (AISI 1006), low-carbon ferroalloys and reactive-grade alloying elements. The steel was cast into big-end-down ingot moulds of 102 mm – 150 mm. The steel ingots were solution treated at 1250 °C and held for 3 h prior to rolling. The cast steel was hot rolled in a lab scale, 50-ton, two-high reversing mill (at a temperature range of 1150 °C – 900 °C) to a reduction area ratio of 6:1.

Specimens were cut from bulk for chemical analysis and optical determination of the mean grain size. A few thin foil specimens for TEM were also made. These samples were punched in 3 mm discs to be prepared metallographically and ultrasonically cleaned. The discs final thickness ranged from 50 to 70 µm. The thin foils were

Table I. Chemical composition of the niobium microalloyed steel (wt %)

Tabla I. Composición química del acero microaleado al niobio (% en peso)

C	Mn	Si	S	P	N	Nb
0.019	0.45	0.038	0.026	0.013	0.0075	0.048

achieved by electro-polishing using an electrolytic solution of 5 % perchloric acid and 95 % ethanol at −30 °C. The thin foils were analyzed in a PHILLIPS CM200 TEM operated at 200 kV. The chemical composition was determined using an ultra thin window EDAX spectrometer. The microstructure was observed in bright field mode. The precipitates and the surrounding steel matrix have been analyzed with a GATAN Digi-PEELS 766 spectrometer in diffraction mode. The conditions used during collections of EELS spectra in TEM were an energy dispersion of 0.1 and 0.3 eV /channel, a collection semi-angle of 10 mrad, and an entrance aperture of 3 mm. The beam spatial resolution achieved was about 1.1 nm. The energy calibration of the core-loss region and the measurement of the energy drift during data acquisition were performed by collecting zero-loss spectra before and during collecting zero-loss spectrum. The major source of error in the energy calibration was found in the energy drift of the zero-loss peaks. The C-K edge spectrum was acquired immediately to the spectrum collection from the Nb-M zone. Finally, the shape and size were quantified based on the TEM micrographs with image analysis software.

3. RESULTS AND DISCUSSION

3.1. TEM characterization of precipitates

The final matrix microstructure is typical of recrystallized austenite with a mean grain size of ~16 µm, as a result of the thermomechanical treatment[14] described in section 2.

TEM examination of the particles was conducted by thin foils. Figure 1(a-c) are bright field STEM images of typical precipitates. Figure 2 shows the sizes distribution of the particles ranging from 10 to 250 nm. The density of particles are about 25 particles/µm². The largest number of precipitates consisted of polyhedral shape 10–50 nm niobium carbide, located both in the matrix and at grain boundaries. The medium size of this principal group of precipitates was about 26 nm. Cubic precipitates with plane faces and round vertices, varying from 60–120 nm, were found at both grain boundaries and in the steel matrix and their medium size was 76 nm. Small quantities of 150–250 nm cuboids NbC precipitates with MnS heterogeneously nucleated were observed in the steel matrix. The presence of nanometric, cuboids particles in niobium microalloyed steel is representative of the
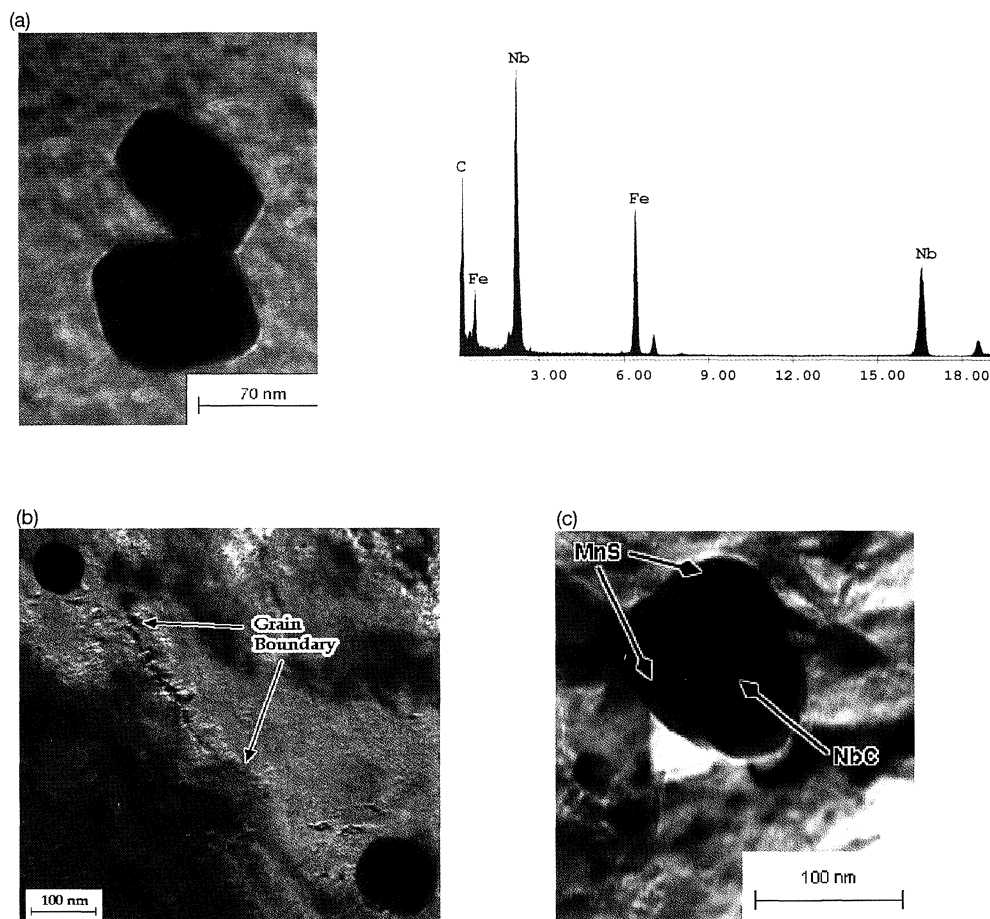
Figure 1. Bright field TEM micrograph corresponding to NbC precipitates. a) Polyhedral shapes and EDX spectrum; b) cuboids shapes at grain boundaries; c) MnS heterogeneously nucleated on NbC precipitates.

Figura 1. Micrografía de MET en campo claro correspondiente a precipitados de NbC. a) Formas poliédricas y espectro de dispersión de energías; b) Formas cuboides; c) MnS nucleado heterogéneamente sobre precipitados de NbC.
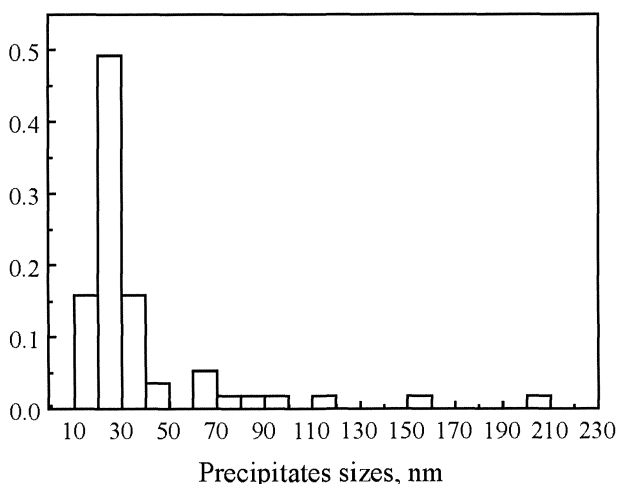

Figure 2. Frequency distribution of precipitates sizes.

Figura 2. Distribución de frecuencia de tamaños de precipitados.

deformation induced precipitation, which is mainly responsible for strengthening the steel.

3.2. EELS analysis

The EELS spectrum acquired was processed to model and then subtract the background. To model the background, first, a portion of the spectrum was defined. The region was chosen between Nb M-edge and C K-edge peaks because it would permit a good extrapolation to the last channel of the spectrum[15]. Although the power-low model may describe such selected region with good fitting, it was found that the background subtraction is of less magnitude than the calculated with a non-linear model of the form $\beta_0 + \beta_1 \, 2^{-t/\theta}$ [16] (Fig. 3).

Results of the EELS analysis of the precipitates revealed that the C-K edge collected from a large
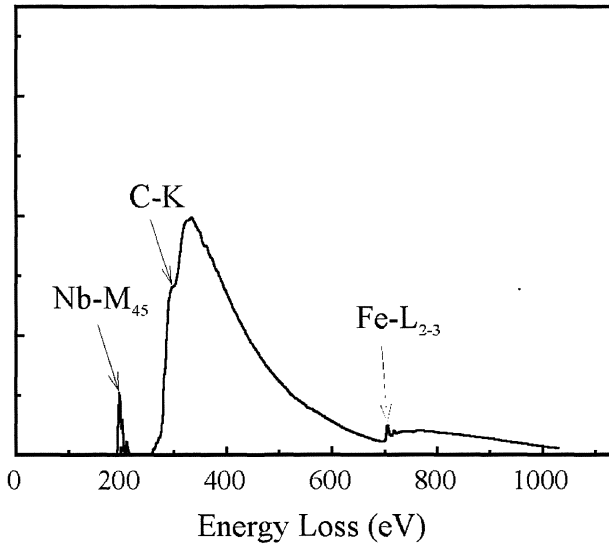
Figure 3. NbC precipitate loss energy spectra in diffraction mode. The background was removed using a like-potential model.

Figura 3. Espectro de pérdida de energía de precipitado de NbC obtenido en modo de difracción. El ruido de fondo se eliminó empleando un modelo de tipo potencial.

number of precipitates appears like the one collected from a single crystal of NbC [13]. With a focused electron beam on every single particle, the X-ray microanalysis showed the presence of niobium and carbon. However, the presence of nitrogen in more than 20 thin foils samples was not detected, neither in solid solution nor associated to a compound.

Using the beam energy loss generated by passing through the precipitates, it has been possible to separate out the carbon contribution from steel matrix and infer its chemical nature. In the low-loss energy region, the background falls smoothly but leaves as peaks the atoms ionization edges, as shown in figure 3. For the Nb $M_{4,5}$-edge, a peak at about 200 eV is presented. However, the EELS analysis in the steel matrix surrounding the precipitates reveals no presence of niobium atoms in the iron lattice. This result is evidence for the chemical environment of the niobium atoms, exhibiting the fine structure of the energy loss spectrum that reveals chemical bounding characteristic of a compound.

A confirmation of this outcome comes within a more detailed study of the absorption edge for the carbon. EELS spectrum was acquired in at least 20 precipitates as well as in the steel matrix. Figure 4 shows a superimposing of the carbon ionization edge in both regions. In the steel matrix, the peak for carbon absorption edge (C K: 292.2 eV) is of
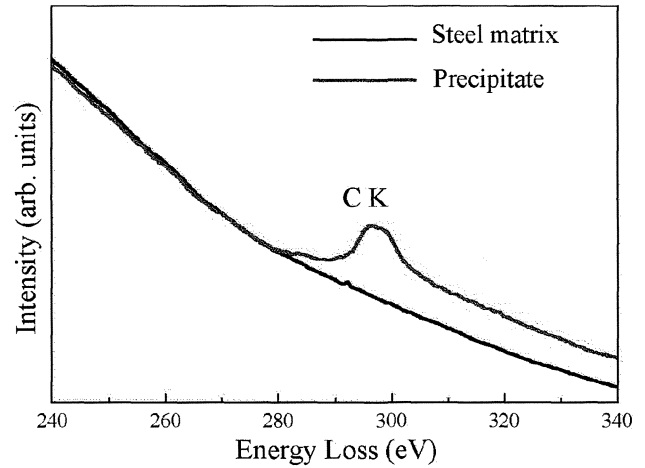

Figure 4. Superimposed EELS spectrum at carbon ionization edges from regions in steel matrix and precipitate. Reprinted with the permission of Microscopy Society of America.

Figura 4. Espectros superpuestos de EELS en los bordes de ionización del carbono de zonas en la matriz de acero y del precipitado. Reimpreso con el permiso de Microscopy Society of America.

low intensity, thinner and slightly displaced to the left in comparison with the one acquired in the precipitate (C K: 296.4 eV). This displacement was taken as an evidence that carbon in precipitates is forming a compound with niobium.

Figure 5 is a comparison between the spectrum from the steel matrix and from the precipitates corresponding to the iron ionization edges (L_3: 708 eV, L_2: 721 eV). A detailed study of the energy loss spectra verifies that the relative
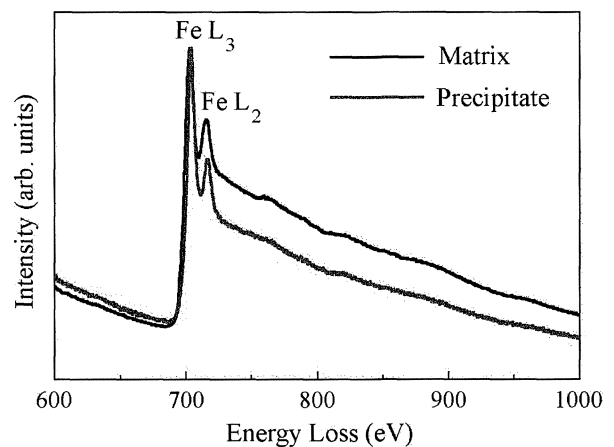

Figure 5. Superimposed EELS spectrum at iron ionization edges from regions in steel matrix and precipitate. Reprinted with the permission of Microscopy Society of America.

Figura 5. Espectros superpuestos de EELS en los bordes de ionización del hierro de zonas en la matriz de acero y del precipitado. Reimpreso con el permiso de Microscopy Society of America.

191

intensity of the peaks corresponding to the L_2 and L_3 edges at both zones is displaced slightly. Apparently there is a change in the iron electronic structure at the interface precipitates-steel matrix[17]. However, this change could not be quantified and interpreted and further studies with better resolution are required[18].

4. CONCLUSIONS

TEM was used to determine the size, shape, number and localization of the nanometric precipitates in a niobium microalloyed steel.

The precipitates are NbC of cuboids shape, 20–180 nm size, and there were 25 particles/μm^2. Their location is in grain boundaries and in the matrix steel.

The presence of niobium and carbon and no nitrogen atoms in precipitates were confirmed by EELS spectra.

In this very low carbon microalloyed steel, the carbon is present in form of carbide compound.

ACKNOWLEDGEMENTS

REFERENCES

[1] C.A. HERNÁNDEZ, S.F. MEDINA, J.E. MANCILLA y V. BLÁZQUEZ, *Rev. Metal. Madrid* 28 (1992) 369-382.

[2] A. ARTIGAS, M. PÁEZ, Y. HOUBAERT, A. MONSALVE y D. CELENTANO, *Rev. Metal. Madrid* 38 (2002) 339-347.

[3] S.F. MEDINA, *Scri. Mater.* 32 (1995) 43-48.

[4] S.F. MEDINA y J.E. MANCILLA, *ISIJ Inter.* 36 (1996) 1063-1069.

[5] S.F. MEDINA y J.E. MANCILLA, *ISIJ Inter.* 36 (1996) 1077-1083.

[6] L. BÉJAR, C.A. HERNÁNDEZ, J.E. MANCILLA, F. ESPINOSA y F. PARAGUAY, *LatinAm. J. Met. Mater.* 21 (2002) 21-26.

[7] A.C. KNEISSI, C.I. GARCIA y A.J. DEARDO, *HSLA Steels: Processing, Properties and Applications*, Beijing, China, 1992, G. Tither and Z. Shouhua (Eds.), The Minerals, Metals & Materials Society, 1992, pp. 99-105.

[8] B.S. NELSON, F. ZHANG y J.D. BOYD, *Thermec'97. International Conf. on Thermomechanical Processing of Steels & Other Materials*, 1997, T. Chandra, y T. Sakai (Eds.), The Minerals, Metals & Materials Society, 1998, pp. 491-497.

[9] R.M. POTHS, R.L. HIGGINSON y E.J. PALMIERE, *Scri. Mater.* 44 (2001) 147-151.

[10] J.E. MANCILLA, L. BÉJAR, C.A. HERNÁNDEZ y F. PARAGUAY, *Jornadas SAM–CONAMET–AAS*, Misiones Argentina, 2001, pp. 541-574.

[11] H.-O. ANDREN, *Micron.* 32 (2001) 713-719.

[12] J.A. WILSON y A.J. CRAVEN, *Ultramicroscopy* 94 (2003) 197-207.

[13] T. EPICIER, E. COURTOIS, J.C. LEBOSSE, M.C. CHEYNET, C. SCOTT y P. BARGES, *Workshop EELS of Steels and Alloys*, Research Institute for Electron Microscopy, Graz University of Technology, Austria, 2003, p. 7.

[14] C. CAMURRI, *Rev. Metal. Madrid* 39 (2003) 132-139.

[15] D-R LIU y L.M. BROWN, *J. Microscopy* 147 (1987) 37-49.

[16] W.N VENABLES y B.D. RIPLEY, *Modern Applied Statistics with S-PLUS*, Ed. Springer-Verlag, New York, EUA, 1999, pp. 241-280.

[17] A.J. CRAVEN, K. HE, L.A.J. GARVIE y T.N. BAKER, *Acta Mater.* 48 (2000) 3857-3858.

[18] C.A. HERNÁNDEZ, L. BÉJAR, J. E. MANCILLA y F. ESPINOSA, *Micros. Microanal.* 8 (2002) 624-625 CD.