Microsc. Microanal. 12, 331–334, 2006
DOI: 10.1017/S1431927606060466

Microscopy AND Microanalysis

Practical Aspects of Carbon Content Determination in Carburized Steels by EPMA

Florence Robaut,[1,*] Alexandre Crisci,[1,2] Madeleine Durand-Charre,[2] and Danielle Jouanne[3]

[1]*Consortium des Moyens Technologiques Communs, INPGrenoble, BP 75, 38402 Saint Martin d'Hères cedex, France*
[2]*Laboratoire de Thermodynamique et Physicochimie des Matériaux (UMR INPG-CNRS 5614), BP 75, 38402 Saint Martin d'Hères cedex, France*
[3]*Renault S.A., Direction de l'Ingéniérie des Matériaux, Service Analyses Physico-chimiques (64160), 78288 Guyancourt cedex, France*

Abstract: The carbon contents in carburized steels were investigated by electron probe microanalysis (EPMA) for a range of carbon levels in the solid solution less than 1 wt%. This article describes the difficulties encountered with the classic analytical procedure using the k ratio of X-ray intensities and the $\phi(\rho z)$ model. Here, a suitable calibration curve method is presented with emphasis on the metallographic study of standard specimens and on the carbon decontamination of samples.

Key words: carburized steel, electron probe microanalysis, carbon analysis

INTRODUCTION

A new carburization process, based on a low pressure plasma technique, is applied in the steel industry and the process conditions are optimized taking into account the carbon content measurements. The range of the carbon level of the investigated steels is less than 1 wt%. Electron probe microanalysis (EPMA) is a powerful technique for the investigation of the carbon content in carburized steels. However, practical problems are encountered, in particular because the X-ray emission of carbon is low and the absorption of C Kα radiation is high in different matrices (Bastin & Heijligers, 1986; Goldstein et al., 1992; Pouchou, 1996). The aim of this work was to determine a suitable procedure for carbon microanalysis in steels by EPMA.

INSTRUMENTATION

Carbon was analyzed using a Cameca SX50 (Cameca: www.cameca.fr) and a JEOL JXA 8900R microprobe (JEOL: www.jeol.com), both with a tungsten/silicon multilayer monochromator (2d spacing = 9.5 and 9.7 nm, respectively, for the SX50 -crystal PC2- and the JXA -crystal LDE2-). The Cameca SX50 is a piece of equipment from the Consortium des Moyens Technologiques Communs (CMTC), Institut National Polytechnique de Grenoble, and the JEOL JXA 8900R is from the Service Analyses Physico-chimiques, Renault SA. Microprobe automation on both microprobes is performed with SAMx software (SAMx: www.samx.com).

OPERATING CONDITIONS

One major problem in carbon measurements is the carbon surface contamination due to the cracking of residual organic molecules under the action of the electron beam. The organic molecules come from the vacuum greases, the residual oil vapors of the pumping equipment, and the contamination of the specimen itself. In this study, a liquid nitrogen cooling trap and a low-pressure jet of gas (oxygen or air) onto the specimen were used to reduce the carbon contamination. Moreover, the mounted standards and samples were mechanically polished just before their introduction into the microprobe chamber. The final polishing was performed with colloidal silica or alumina solution, followed by a very careful ultrasonic cleaning.

Carbon was analyzed at an accelerating voltage ranging between 10 and 13 kV with a beam current between 300 and 400 nA for improved counting statistics. Although multilayer monochromators are less sensitive to higher-order peaks, a rather narrow window for the pulse height analyzer (PHA) was selected. Thus, the PHA was optimized to reject the usual higher-order peaks: Ni Lα $n = 3$,

Received May 13, 2005; accepted April 18, 2006.
**Corresponding author*. E-mail: florence.robaut@cmtc.inpg.fr

Cr Lα $n = 2$, Mn Lα $n = 2$, Fe Lα $n = 2$, Fe Lα $n = 3$, Fe Ll $n = 2$.

ANALYTICAL PROCEDURE USING THE k RATIO OF X-RAY INTENSITIES AND THE $\phi(\rho z)$ MODEL

The classic quantitative analytical procedure using the ratio of measured intensities of the C Kα line from the sample and the standard was first tested. Matrix corrections were made using the PAP $\phi(\rho z)$ model (Pouchou & Pichoir, 1986). Different carbon standards were tested (diamond, cementite, carbon solid solution in steels, $C = 1$ wt%). The background intensity was measured, either at the left- and right-hand sides of the carbon peak or on a pure iron standard at the position of the carbon peak. As the chemical bonding may induce wavelength shifts or peak shape alteration, this effect was also taken into account in the $\phi(\rho z)$ model with correction factors (area peak factors) for C measurements on diamond and cementite standards. The area peak factor is the ratio of the k ratio obtained by using the integral intensity of the peak and the k ratio obtained by using the peak intensity. Carbon measurements obtained with this classic procedure on a specimen with a known composition were not reproducible with any of these experimental conditions. Moreover, they did not fall within the range of the expected values. This can be explained by numerous factors (Bastin & Heijligers, 1986; Goldstein et al., 1992; Pouchou, 1996): the low peak-to-background intensity ratio, the difficulties encountered with background measurements due, in particular, to the fact that the Fe high-order peaks from the matrix are not completely removed by the differential mode, and the sensitivity to pulse shifts in the differential mode of the PHA for large differences in count rates between standard and the sample.

ANALYTICAL PROCEDURE USING THE CALIBRATION CURVE METHOD

Another analytical procedure is based on the determination of a calibration curve for the C Kα line intensity at the maximum of the peak as a function of carbon content in the range of 0–1 wt%. In this procedure, background intensity is not measured. The carbon content of the unknown sample is simply calculated from the regression curve coefficients A and B (counts = A $*$ carbon wt% + B).

Standards Used for the Establishment of the Calibration Curve

A critical point of this method was the choice of steel standards giving reproducible carbon intensity measurements. The standards must be homogeneous on the scale of the C Kα emission volume in steel (0.2 μm in depth and >1 μm laterally, for HV = 13 kV and high beam current). A series of standards with various carbon contents ranging from 0 to 1 wt% was investigated: pure iron, steels with, respectively, 0.42 wt% (42CrMo4) and 0.98 wt% (100Cr6) of carbon. Specific heat treatments were carried out on the standard specimens to obtain a homogeneous carbon content in the matrix. Austenitization treatment at 1000°C for 30 min seems sufficient to completely dissolve the carbides (such treatments are usually performed at 900°C). A subsequent quench transforms austenite into martensite. After the nital etching, metallographic examinations of the as-quenched specimens were carried out to verify the complete dissolution of carbides (Durand-Charre, 2004). To determine the influence of microstructure on the carbon measurement, two sets of samples were investigated in the case of 0.42 wt% carbon steels (42CrMo4). The first one with as-quenched specimens exhibited a characteristic martensitic structure (Fig. 1, left side); the second one with annealed specimens exhibited tempered martensite, that is, ferrite matrix with tiny carbides (Fig. 1, right side). During the tempering treatment, the carbon content decreases in the matrix toward an equilibrium state involving a low carbon ferrite and cementite precipitates. This decrease of carbon content is associated to a global hardness decrease (Table 1). At the first stage of the treatment, carbides are very fine and close. Then, they coarsen, small carbides dissolve, and larger carbides grow. The longer the tempering treatment, the coarser are the carbides relative to a softer matrix. This fact is in agreement with the high dispersion of the carbon measurements observed systematically for the soft specimens (Table 1). However, the average C Kα intensity, shown in Table 1, does not indicate the carbon content in the matrix because this analysis involves an inhomogeneous volume, except in the case of as-quenched martensite.

This metallographic study appeared to be necessary for selecting good specimens able to form a set of homogeneous standards used in the calibration curve method. As an example, the set of standards, used in the CMTC laboratory to determine the calibration curve, consists of pure iron steels with, respectively, 0.2 wt% C (20NiCr Mo2), 0.42 wt% C (42CrMo4), 0.98 wt% C (100Cr6), and 0.99 wt% C (100Cr6). Steel samples are fully martensite. The calibration curve for the determination of carbon content in steels (Fig. 2) is deduced from the C Kα intensity measurements on this set of standards, at 13 keV and 400 nA. It gives the relationship between the C Kα intensity and the carbon content in the steel samples.

Decontamination Procedure

It has been shown that exposure of the samples to the primary electron beam plus oxygen induces carbon decontamination. This effect is exploited in carbon measurements in steel standards and unknown samples. Figure 3 shows the

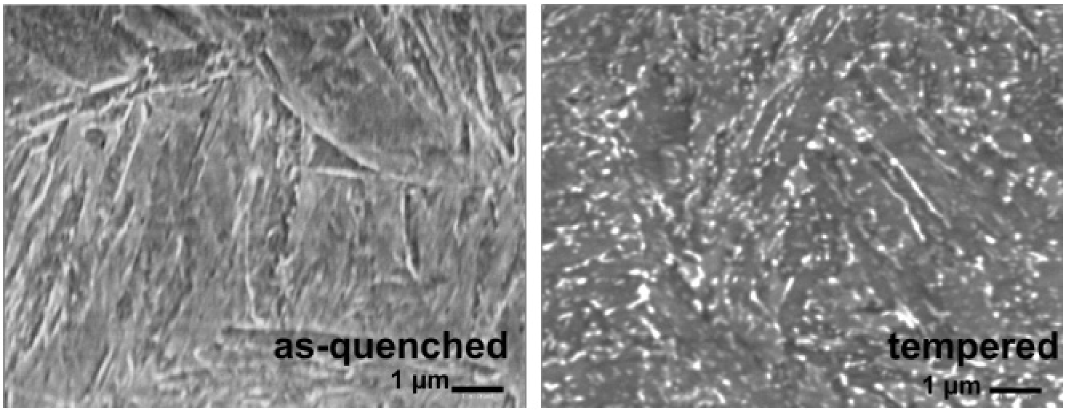

Figure 1. Secondary electron micrographs of two 0.42 wt% carbon steels (42CrMo4) after inital etching. The as-quenched specimen (left side) exhibits a characteristic martensitic structure with fine elongated laths; the annealed specimen (right side) exhibits tempered martensite, that is, a ferrite matrix with tiny carbides precipitated along the previous lath boundaries.

Table 1. Characteristics of Different 0.42 wt% Carbon Steels (42CrMo4)[a]

		Average intensity (C Kα)		
	Hardness HRC	Intensity (counts/s)	Standard deviation	Optical micrograph
As-quenched	>50	2041.9	20.6	Only martensite
Tempered	36–40	2050.2	67.6	Carbides
Tempered	29–30	2004.9	128.8	Carbides

[a] The dispersion of carbon measurements, for 10 analyzed points per sample (standard deviation σ), is correlated to the metallographic observations (Fig. 1) and to the hardness values (CMTC data obtained at 13 kV, 400 nA, with an air jet and a LN_2 cooling trap).

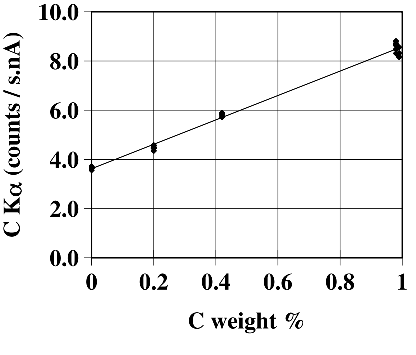

Figure 2. Calibration curve obtained at 13 keV and 400 nA with pure iron and fully martensite steel standards with, respectively, 0.2 wt% C (20NCD2), 0.42 wt% C (42CrMo4), 0.98 wt% C (100Cr6), and 0.99 wt% C (100Cr6) (CMTC data).

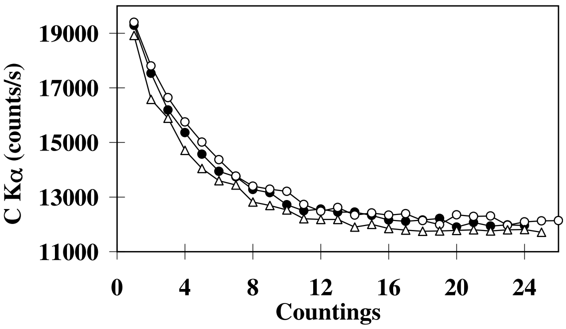

Figure 3. On the same standard (a 1.02 wt% C steel), three series of carbon measurements located at the same point were performed, illustrating the evolution of the decontamination process (Renault S.A. data). Operating conditions were: HV = 10 kV, I = 300 nA, with a LN_2 cooling trap, an air jet, and a 10 s decontamination time between two measurements. C Kα signal is represented as a function of the successive counting times of 10 s performed for the same point of the standard. The different curves are very close showing that the decontamination process is reproducible.

carbon signal variation for successive counting times of 10 s performed at the same point on a C 1.02 wt% standard steel (Renault S.A. data). It can be seen that a decontamination time of 100 s, at least, is necessary before carbon measurement. The three curves shown in Figure 3 correspond to different series of carbon measurements. They demonstrate that the decontamination process is reproducible. For lower C content steel standards, the same behavior was observed with exposure to the electron beam. This effect can be explained by the combined action of the air (or oxygen) jet into the vicinity of the sample with electron bombardment

(Goldstein et al., 1992). Microprobe automation programs developed by SAMx can determine a decontamination time prior to carbon measurement (Thiot, 1995). A statistical χ^2 test, integrated to the acquisition program, is based on the carbon signal variation versus time at each point. This test determines and manages automatically the decontamination process.

It has been found that plasma cleaning of the specimens, prior to their introduction into the microprobe chamber, also reduces carbon contamination. Plasma cleaning should be implemented in the procedure to decrease *in situ* decontamination time.

CONCLUSIONS

Electron probe microanalyzer measurements on steels with known carbon content have shown that accurate quantitative analysis can be obtained with the proposed calibration curve method because the homogeneity of the standards has been carefully verified. Moreover, the problem of adsorbed carbon is solved by an *in situ* decontamination process prior to C Kα signal measurement due to the combined action of air jet and electron bombardment.

ACKNOWLEDGMENTS

The authors acknowledge C. Tassin (LTPCM) for austenitization treatments of the standards and F. Charlot (CMTC) for SEM observations.

REFERENCES

Bastin, G.F. & Heijligers, H.J.M. (1986). Quantitative electron probe microanalysis of carbon in binary carbides. *X-ray Spectr* **15**, 135–150.

Durand-Charre, M. (2004). *The Microstructure of Steels and Cast Irons*. Berlin: Springer.

Goldstein, J.I., Newbury, D.E., Echlin, P., Joy, D.C, Romig, A.D., Lyman, C.E., Fiori, C. & Lifshin, E. (1992). *Scanning Electron Microscopy and X-Ray Microanalysis*. New York: Plenum Press.

Pouchou, J.-L. (1996). Use of soft X-rays in microanalysis. *Mikrochimica Acta Supplementum* **13**, 39–60.

Pouchou, J.-L. & Pichoir, F. (1986). Very light elements X-ray microanalysis. Recent models of quantification. *Journal de Microscopie et de Spectroscopie Electronique* **11**, 229–250.

Thiot, J.F. (1995). *Etalon & Profile Manual, a Trace Analysis Package*. Levens: SAMx S.A.