MÖSSBAUER SPECTROMETRY OF A NOVEL STEEL LC200N WITH HIGH CORROSION RESISTANCE

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Abstract

We present results of the study of structural features of a novel (introduced in 2013) highly corrosion resistant LC 200 N steel, possessing large and stable hardness up to relatively high temperatures and excellent wear resistance. LC200N is a perspective material which can be considered for possible applications in nuclear installations. We have employed Scanning Electron Microscopy/Energy Dispersive Spectrometry (SEM/EDS) and micro X-ray fluorescence analysis (XRF) for sample characterisation and check of the element composition. The samples were investigated both in the as-prepared state, i.e. in form of round plates (thickness ~0.5 mm) after electro-erosive cutting from original rods as well as after polishing both surfaces. SEM/EDS unveiled regions with different Cr concentrations in the steel – bulk material with lower Cr concentration and precipitates with considerably higher Cr concentration. Magnetically active ferrite phases as well as non-magnetic austenite were identified in samples by Mössbauer spectrometry via probe ^{57}Fe nuclei. Contribution of the austenite is only marginal in the non-hardened (annealed/soft) steel, but much higher in hardened one. The complex behaviour of magnetic phases governed by varying number of Cr atoms in the first nearest neighbour shells of the resonant Fe atoms was observed.

1. Introduction

The steel LC200N [1] is a chromium alloyed tool steel with high nitrogen content produced by the PESR (Pressurized Electric Slag Remelting) technology [2]. This production procedure increases purity of the resulting material and refines its microstructure. Compared to standard tool steels LC200N exhibits higher corrosion/wear resistance and toughness as well as higher tempering resistance up to 500 °C still retaining the hardness of 58 - 60 HRc. Its primary advantage rests with an excellent ability to be machined and polished as well as with its high dimensional stability after heat treatment.

In order to understand the effect of the particular alloying elements upon structural characteristics and the description of microstructural arrangement of this material we have employed Mössbauer spectrometry as the principal method of analysis. Complementary supporting information was obtained by SEM/EDX and XRF.

2. Experimental

The coin-shaped samples (25 mm diameter/thickness ~0.5 mm) of the LC 200 N steel were cut by brass wire using electric discharge machining (EDM) [3] from the original rods with the diameter of 25 mm. Two types of samples were studied: (i) hardened – *sample A* and (ii) non-hardened (annealed) – *sample B*. Surface contamination by Cu/Zn (brass) from the cutting wire occurred on the faces of the samples.

Disk samples (A and B) were further thinned by SiC abrasive papers (240 – 2000 grit) under water to the final thickness of ~30-60 μm and polished by a 1.6 μm diamond paste. The final polishing was made by a Wenol® Metal Polish paste to a mirror-like surface, which also completely removed the brass contamination of the surface from the cutting.

SEM/EDS analysis was performed using FEI QUANTA FEG electron microscope with EDAX (Si/Li) EDS system. Surface contamination, chemical composition of the alloy and its homogeneity were checked by XRF spectrometer EAGLE III μ-Probe operated at 40 kV.

^{57}Fe Mössbauer spectra were collected at room temperature in transmission geometry using a standard constant-acceleration spectrometer equipped with a ^{57}Co/Rh source. Calibration of the spectrometer was done by an α-Fe foil (12.5 μm) at room temperature. Spectral parameters were derived by the help of the CONFIT fitting software [4].

3. Results and Discussion

3.1 Scanning Electron Microscopy/ Energy Dispersive Spectrometry

For SEM images the polished surfaces of the samples were only used – see Fig. 1. Two distinct regions are clearly visible: the light grey bulk material is filled by well separated oval-shaped darker particles. The concentrations of Cr and Fe strongly differ: in the bulk material the Cr content is 15±4 % and in the darker particles Cr concentration reaches 50±10 %. The concentration was established by EDS (Energy Dispersive Spectrometry) in 50 points in each area.

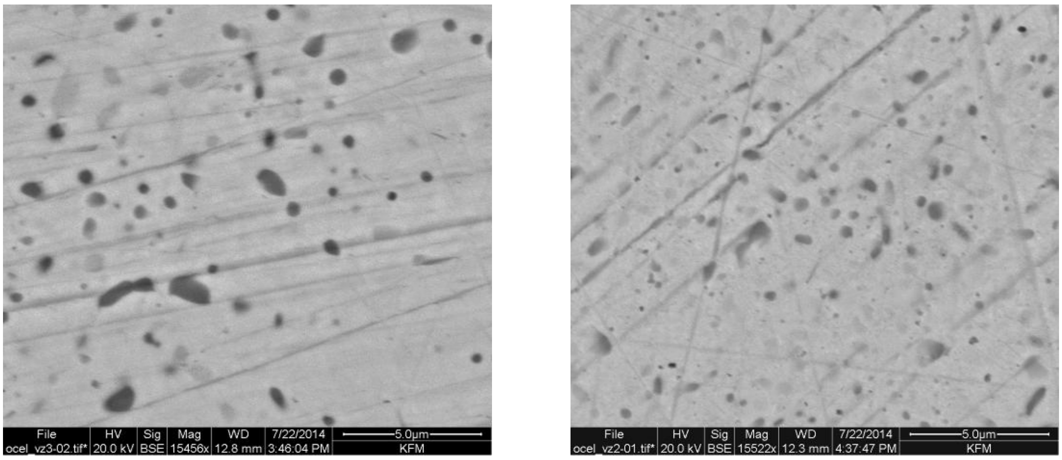

Fig. 1. *SEM images of the polished Sample A - hardened (left) and Sample B – annealed (right).*

3.2 X-ray Fluorescence

The results of XRF analysis are listed in Table 1. They are compared with the nominal composition supplied by the producer of this steel. Relatively good agreement between the data is achieved. It should be noted that XRF analysis provides information also on the presence of other elements, Al, P and V, not specified in the producer's certificate. According to the element XRF mapping the samples were homogeneous.

Table 1. Contents of individual elements from micro XRF compared to the producer's data [1].

source	**element**	**Fe**	**Cr**	**Si**	**Mo**	**Al**	**Mn**	**Ni**	**P**	**V**	**Cu**
XRF	%	79,40	16,10	1,00	1,40	0,70	0,80	0,20	0,20	0,13	0,10
producer catalog	min. %	-	14,00	-	0,85	-	-	-	-	-	-
	max %	-	16,00	1,00	1,10	-	1,00	0,50	-	-	-

3.3 *Mössbauer Spectrometry*

Transmission room temperature ^{57}Fe Mössbauer spectra of the hardened (*Sample A*) and non-hardened (*Sample B*) steel samples (foils thickness ~50 μm) are displayed in Fig. 2. In the *Sample A* (Fig. 2a) a huge central line (plotted in black colour) corresponding to austenite dominates over smaller sextuplet. The spectrum of *Sample B* (Fig. 2b) shows clear six-line pattern with only traces of a central single absorption line (again shown in black in its central part). The six-line patterns in both spectra are assigned to magnetically ordered ferrite phase. They were fitted by 8 and 7 sextets for *Sample A* and *Sample B*, respectively. Decomposition of the sextuplet part of spectra to components is plotted in Fig. 2 in different shades of grey colour.

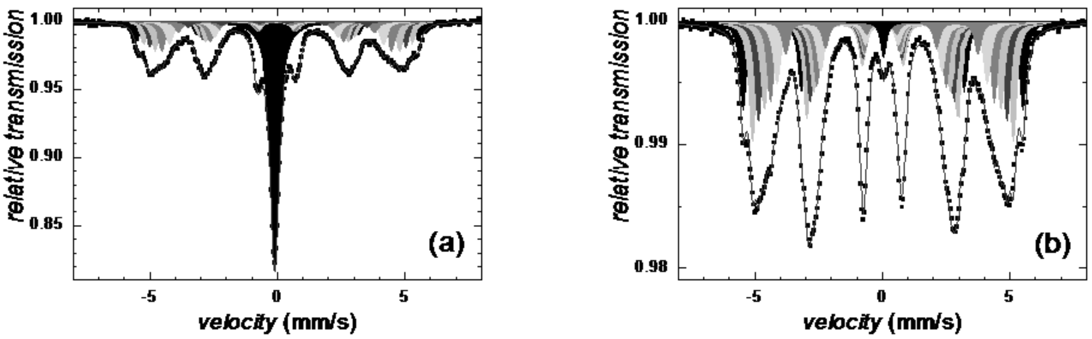

Fig. 2. ^{57}*Fe room temperature Mössbauer spectra of Sample A (a) and Sample B (b). See text for details.*

The sextets in Mössbauer spectra represent those Fe atoms which have different number of Cr nearest neighbours (nn) in the crystallographic lattice with 9 possibilities as the maximum number. Their respective shares can be calculated using the binomial distribution:

$$P(n) = \frac{8!}{n!\,(8-n)!} \cdot x^{n} \cdot (1-x)^{(8-n)}$$

, *n*-number of Cr nn of Fe atom (0-8), *x*-Cr concentration. (1)

We have considered $x = 0.15$ and $x = 0.50$ for the two distinct Cr regions as determined by EDS (Fig. 1). Consequently, the resulting site occupations were derived as a linear combination of these two distributions. Such approach assumes that in the Fe crystallographic lattice only Cr atoms are taken into account with two different concentrations *x*. This simplified procedure is possible as the relative fractions of other elements than Cr in the investigated steel are negligible (see Tab. 1). It was thus not necessary to use a multinomial function that should be applied if the system contains more than two kinds of atoms [5].

The calculated binomial distributions are plotted in Fig. 3 as a function of the number of Cr nn for $x = 0.15$ (light grey) and $x = 0.50$ (grey). Maximum probability is found for 1 Cr nn in the former and 4 Cr nn in the latter case. The results of experimental Mössbauer spectra refinements, i.e. the fitted relative fractions of the individual sextets are shown by black solid circles. These experimental data (black circles) were compared with a linear combination of the two distributions plotted in Fig. 3 by black dashed line and squares.

The ratio of the two binomial distributions (corresponding to Cr contents $x = 0.15$ in the bulk material and $x = 0.50$ in precipitates) was determined to be 70:30 in *Sample A* and 47:53 in *Sample B* (Fig.3).

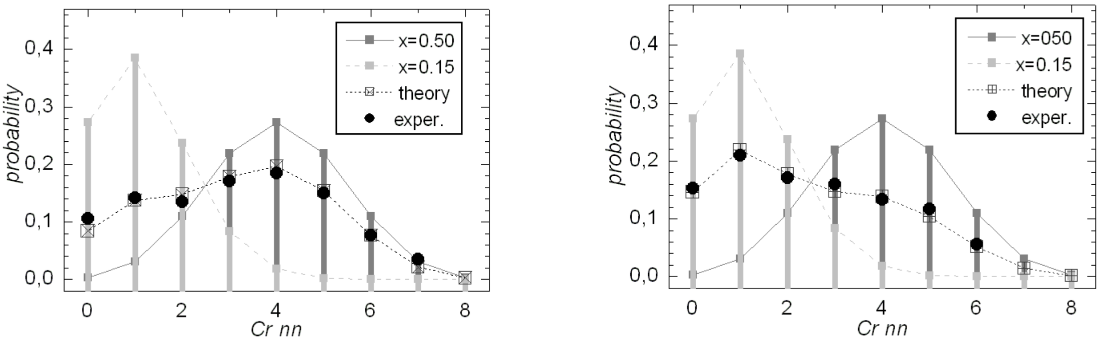

Fig. 3. *Binomial distributions of Cr nn probabilities calculated for the two Cr regions with concentrations x = 0.15 and x = 0.50 and their combination compared with experimental values from Mössbauer spectra of Sample A (a) and Sample B (b). See text for details.*

The Mössbauer spectra were evaluated taking only those sextet components whose relative contributions established from the overall probability distribution were higher than 1.5 % as this is the limit for reliable determination. Considering this constrain we have used 8 and 7 sextets to fit the magnetically ordered parts of the Mössbauer spectra for *Sample A* and *Sample B*, respectively. As seen from Fig. 3, they represent those Fe atoms that have n Cr in their nearest shell with $n = 0$ up to 7 and 6, respectively.

Mössbauer hyperfine spectral parameters were refined in the course of the fitting procedure for all components. The estimated errors are ±0.048 mm/s for the quadrupolar shift *QS*, and ±0.16 T for the hyperfine field B_{hf}. Typical values of line widths varied from 0.26 mm/s up to 0.36 mm/s. They suggest that the structure is well ordered and is only slightly disturbed by the presence of foreign atoms. This assumption is confirmed by the almost zero values of the quadrupolar shift irrespective of the number of Cr nearest neighbours.

Table 2 Hyperfine field per one Cr atom in the nearest neighbour shell of resonant ^{57}Fe atom.

	Cr nn	0	1	2	3	4	5	6	7
Sample A	B_{hf}	34,23	32,64	31,15	29,8	27,98	26,03	23,9	21,67
Sample B	B_{hf}	34,11	31,77	30,27	28,8	27,2	25,54	23,33	

The hyperfine field is considerably affected by the number (and type) of the nn of the resonant ^{57}Fe nuclei. The increase and/or decrease of B_{hf} by increasing the number of nn is generally linear:

$$B_{\mathrm{hf}} = a + b \times (\mathrm{nn}), \qquad (\mathrm{nn}) = 0 - 8 \qquad (2)$$

The symbol (nn) is number of Cr atom in the nearest neighbourhood of Fe atom. The coefficient a of the linear fit to our experimental data of hyperfine fields (Fig. 4) represents

B_{hf} for zero nearest neighbours (analogous to α-Fe with B_{hf} ~ 33 T) and b is the field decrement per 1 Cr nn.

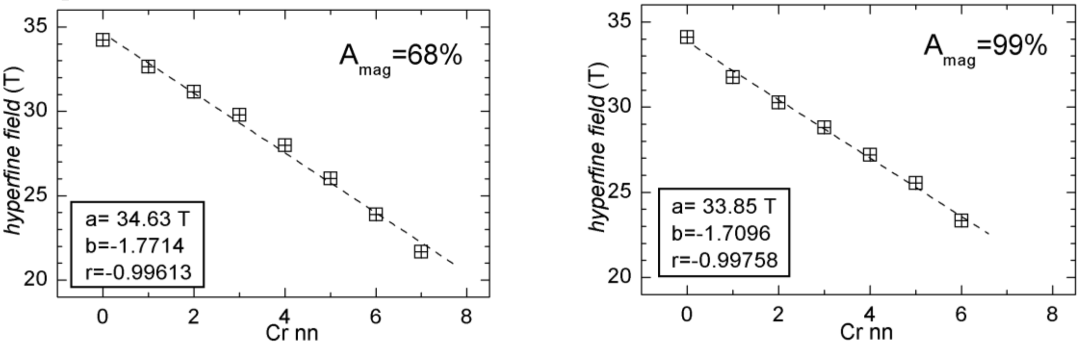

Fig. 4. *Hyperfine fields of the sextets from Mössbauer spectra of the Sample A (left) and Sample B (right) plotted against Cr nn. Dashed lines represent linear fits to the displayed data.*

Though in the hardened steel (*Sample A*) smaller content of the magnetically ordered phase was found (~68 %) B_{hf} at 0 Cr nn derived from the linear fit is higher (34.63 T) in comparison with non-hardened steel (*Sample B*) containing ~99 % of ferrite magnetic phase and displaying hyperfine field equal to 33.85 T. Field decrements are nearly similar in both samples with an average decrease of hyperfine field of ~1.74 T per one Cr atom in the nearest neighbour shell of resonant ^{57}Fe atom.

To finalize the Mössbauer spectrometry studies we should mention that presence of austenite was identified in both samples. It was expressed by the presence of one singlet Mössbauer component. While in the hardened steel (*Sample A*) it amounted to ~32 %, only a minor contribution of austenite (~ 1 %) was found in *Sample B,* i.e. in non-hardened steel.

4. Conclusions

The novel LC 200 N steel could be considered as an appropriate candidate for various critical applications in particular under demanding conditions that frequently occur in nuclear installations.

Structural features of this steel were studied by SEM / EDS technique. Regions with different Cr concentrations were unveiled. The declared Cr content in the producer certificate is between 14 and 16 %. Though the bulk material has shown an average Cr concentration of ~15 %, in good agreement with the producer data (14-16 %), precipitates with considerably higher Cr concentration of ~50 % were identified.

Employing ^{57}Fe nuclei as local probes both structural and magnetic features of the steel were investigated by Mössbauer spectrometry. It was possible to identify magnetically ordered ferrite as well as non-magnetic austenite phases. Contribution of the non-magnetic austenite phase is only marginal and amounts to ~1 % in the non-hardened steel but in the hardened steel it equals ~32 %.

The behaviour of the magnetically ordered phases is governed by varying number of Cr atoms in the first nearest neighbour shells of the resonant Fe atoms. Taking into consideration the results of Scanning Electron Microscopy, two structurally different regions with noticeably distinct Cr concentrations were assumed in the physical model for evaluation of the Mössbauer spectra. A linear combination of two binomial distributions corresponding to the two different Cr concentrations was used to describe the probabilities of occurrence of Cr atoms in the Fe nearest environment. The achieved results indicate that in the hardened steel the relative ratio of regions with ~15 % of Cr to those with ~50 % Cr is 70:30 while in the non-hardened one their shares are almost equal (47:53).

Acknowledgement

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