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ORIGINAL PAPER

Structure of the superficial region and mechanical properties of nitrided cast steels

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Abstract. A series of cast steels were subjected to two-stage low-temperature nitriding. Mössbauer, XRD and mechanical investigations were carried out for both as-cast and nitriding materials in order to determine phase composition (especially the content of γ'-Fe_4N and ε-$Fe_{2\text{-}3}N$), microhardness of the superficial region as well as tribological properties. It has been stated that the relative content of iron-nitrogen phases strongly depends on chemical composition of the cast steel and the effective thickness of the surface layer comprising iron nitrides is less than 0.015 mm. Considerable increase of surface microhardness and wear resistance of nitrided specimens in comparison with their as-cast counterparts has been observed. It has been found that the values of microhardness of nitrided samples at the surface are above twice larger than those in the core.

Key words: cast steel • microhardness • Mössbauer spectroscopy • nitriding • wear resistance

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Introduction

Durability of machine elements made of steel or cast steel concerning abrasion resistance depends on many parameters. Chemical composition of an initial material, heat and chemical treatment as well as production technology influence the structure of surface layer and superficial region and, consequently, determine mechanical features such as hardness or tribological properties. Profitable modification of some mechanical characteristics can be achieved, for instance, by various technologies of surface nitriding [3–11, 13]. Up to now, only few articles have been published regarding properties of nitrided cast steels [1, 2, 12]. The main subject of this paper is a study of the influence of cast steel nitriding on phase composition and microstructure of the surface layer and also mechanical properties: microhardness and tribological characteristics.

Materials and experimental methods

The object of investigations is a series of four medium- and highly alloyed cast steels. Chemical composition of the materials is presented in Table 1. The specimens have nearly similar carbon content, but different percentage of other alloying elements, particularly chromium. The cast steels were subjected to the procedure of low-temperature, two-stage nitriding realized in the Institute of Precision Mechanics in Warsaw. In the first

Table 1. Real content of alloying components of investigated cast steels (in wt.%)

Sample	C	P	S	Si	Mn	Ni	Cr	Mo	V	Cu
A	0.46	0.024	0.009	0.44	0.52	0.7	1.0	0.44	0.52	1.13
B	0.38	0.022	0.001	0.23	0.36	0.61	7.4	0.47	0.2	1.6
C	0.40	0.023	0.001	0.22	0.36	0.64	7.5	0.44	0.2	1.7
D	0.38	0.028	0.006	0.45	0.44	0.77	15	0.48	0.21	1.8

stage the material was treated for four hours in pure ammonia at 480°C, whereas the second one was carried out for 16 h, when the cast steel was annealed at 530°C in a mixture of ammonia (40%) and previously dissociated ammonia (60%). Conversion electron Mössbauer spectroscopy (CEMS) based on ^{57}Fe was employed in order to identify phase composition of the surface layer and superficial region in both as-cast and nitrided samples. Mössbauer measurements were realized using a ^{57}Co(Rh) source of gamma radiation and a gas-flow CEMS detector supplied with a He + 4% CH_4 mixture. The source of gamma photons was placed on the head of a vibrator moving in a constant acceleration mode. Mössbauer spectra were fitted by the use of program NORMOS that utilized the conventional least square procedure with additional smoothing terms.

Structural investigations were performed using X-ray diffraction (XRD) for testing phase composition of the superficial region. They were carried out at room temperature, by means of a powder X-ray diffractometer (Broker D8 Discover) using filtered CrKα radiation (λ = 0.228970 nm), in the angle range $20^{o} \leq 2\Theta \leq 150$.

In order to analyse the distribution of nitrogenous phases over the regions situated in different depth d under the surface, CEMS studies were performed (for nitriding cast steels) after sequential manual rub of several layers up to $d \leq 0.02$ mm. The measurements of actual width of the specimen were carried out by means of a Carl Zeiss Jena optimeter with an accuracy of ±0.001 mm.

Investigations of microhardness of the surface as well as microhardness depth profile were carried out using the Vickers method (with hardness tester 401 MVD) with stress equal to 2.94 N. Friction tests were performed by the use of a tester TT-02LCH based on the friction machine SMC-2. The tests were carried out at room temperature; constant stress equal to 5.3 N was applied.

Results and discussion

Phase analysis

Phase composition of the superficial region has been investigated both by XRD and CEMS. The effective depth of penetration of X-ray amounts from several tenths to tens micrometers, depending on the radiation wave length, the kind of material and the Bragg's angle. Therefore, structural XRD analysis is weakly sensitive to changes of phase composition in the range less than 1 μm. Nevertheless, it delivers substantial evidence concerning crystal structure in the superficial region. Integral CEMS technique consists in detection of electrons, previously emitted as a result of recoil-less de-excitation of the Mössbauer nuclei (in our case ^{57}Fe), then the penetrated range is limited by the electron energy. Accordingly, CEMS yields information from the layer of thickness up to 300 nm, but 65% of electrons originates from the surface layer of thickness 90 nm. Therefore, it enables selective investigations depending on depth of the studied layer under the original surface, with the resolution about 100 nanometers.

X-ray diffraction studies of the as-cast samples evidence the prevalence of α-Fe phase and vestigial content of austenite. Diffraction patterns obtained for nitrided cast steels are shown in Fig. 1. They point to the presence of iron nitrides in all investigated materials. However, while γ'-Fe_4N of cubic crystal lattice dominates in samples A–C, in the cast steel D (containing the larger percentage of chromium) only a small amount of hexagonal phase ε-Fe_2N has been found. The XRD results comprising identified phases and derived crystal lattice constants are presented in Table 2.

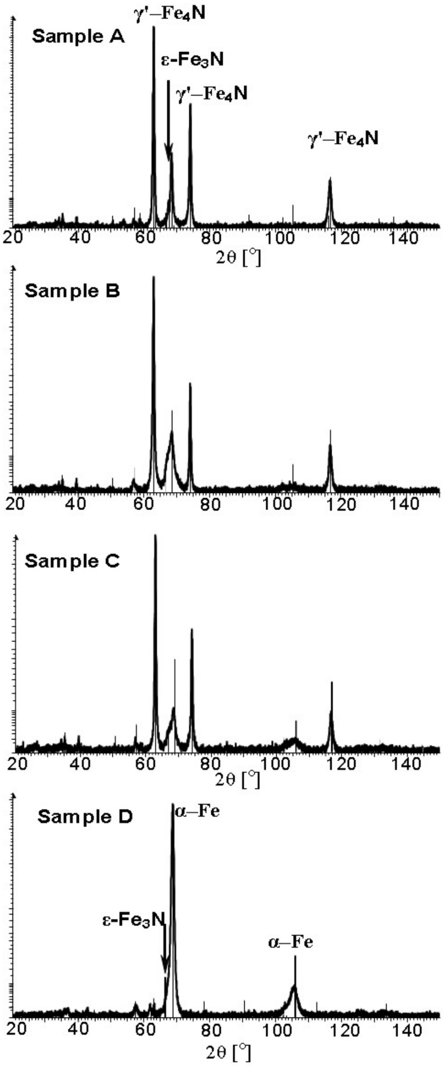

Fig. 1. XRD patterns obtained for nitrided cast steels. Some main peaks of identified phases are shown at the pictures.

Table 2. Crystal lattice constants of identified phases derived from XRD patterns obtained for nitrided cast steels (with uncertainty ±0.00010 Å)

Sample	Phase			
	α-Fe	γ'-Fe_4N	ε-Fe_3N	ε-Fe_2N
A	a = 2.88014 Å	a = 3.79947 Å	$a = b$ = 4.66800 Å c = 4.36200 Å	–
B	a = 2.87536 Å	a = 3.79947 Å	–	–
C	a = 2.86700 Å	a = 3.79790 Å	–	–
D	a = 2.86700 Å	–	–	$a = b$ = 4.76506 Å c = 4.38118 Å

Mössbauer spectra collected for as-cast samples (presented in Fig. 2a) have a shape of more or less broaden sextet with small other additive components. It corresponds to the predominant phases: martensite and α-Fe, that in the fitting procedure are represented by a set of several Lorenzian sextets corresponding to different inequivalent positions of iron atoms in the crystal structure. Besides them, a singlet with an isomer shift of about –0.10 mm/s originated from austenite is visible in the central part of the spectra, relative content of which is about several percent. Distribution of iron atoms over the mention phases derived under the assumption, that the Debye-Waller factor of different phases has a similar value, is presented in Table 3.

Mössbauer spectra collected for nitrided cast steels (Fig. 2b) reveal real changes in phase composition of the surface layer compared with the as-cast samples. Preliminary analysis of the spectra as well as XRD results evidence that, besides of α-Fe and martensite, also iron nitrides: γ'-Fe_4N and ε-$Fe_{2-3}N$ have to be taken into account in the course of the fitting procedure. The nitride γ'-Fe_4N is represented in the spectra by a set of three sextets, corresponding to the three possible surroundings of iron atoms in the crystal lattice (listed

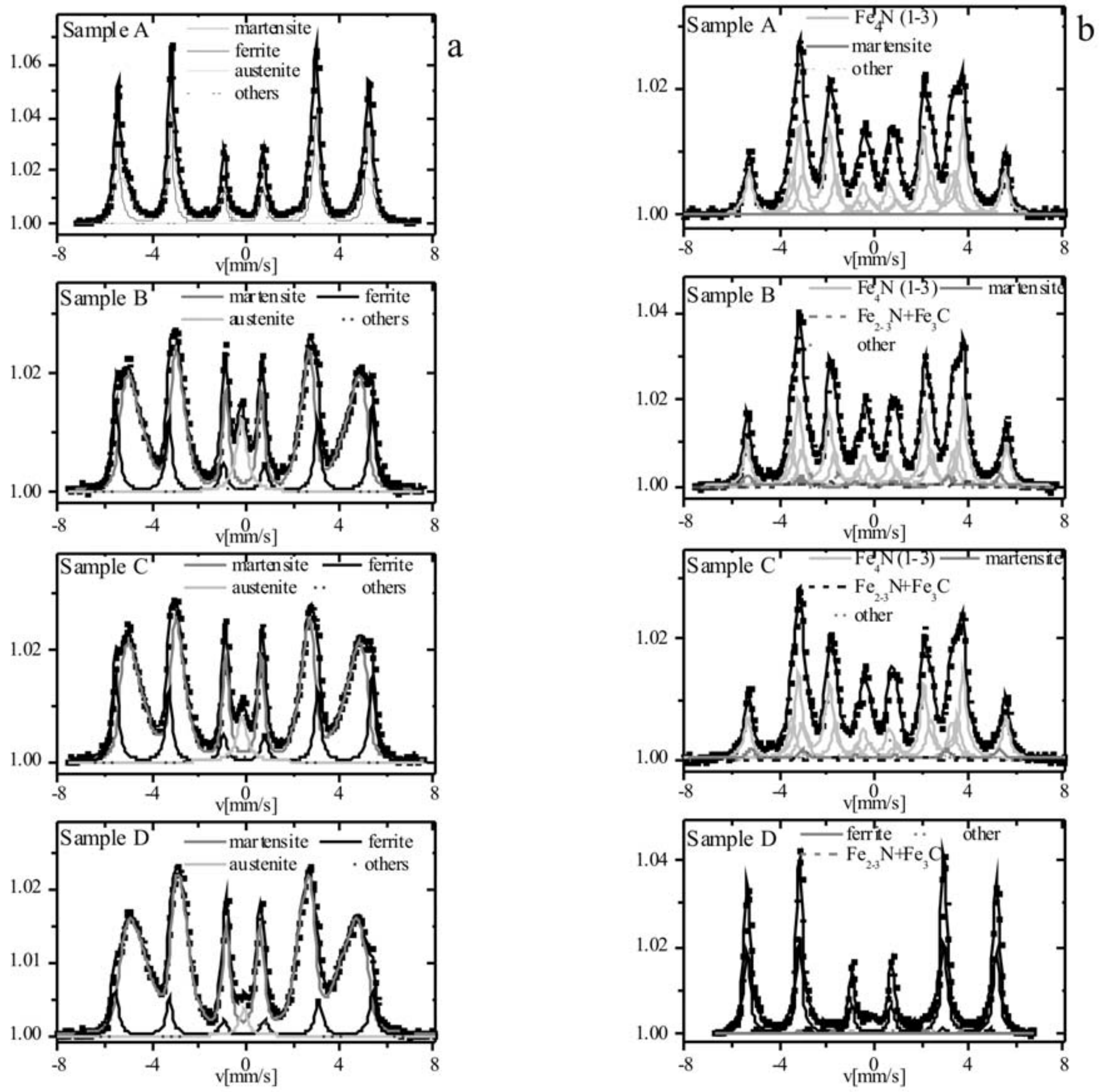

Fig. 2. Mössbauer spectra collected for as-cast (a) and nitrided (b) cast steels.

Table 3. Distribution of iron atoms over different phases derived from CEMS in % (a.c. – as-cast, nitr. – nitrided)

Sample	A		B		C		D	
	a.c.	nitr.	a.c.	nitr.	a.c.	nitr.	a.c.	nitr.
Martensite	60	1	70	6	73	6	89	–
Ferrite	35	–	21	–	20	–	8	90
Austenite	2	–	7	–	4	–	2	–
γ'-Fe_4N	–	96(5)	–	82(5)	–	88(5)	–	–
ε-$Fe_{2\text{-}3}N+Fe_3C$	–	–	–	9	–	3	–	8
Other	3	3	2	3	3	3	1	2

Table 4. Hyperfine interactions parameters: magnetic hyperfine field – *B*, isomer shift – IS and quadrupole splitting – QS as well as intensity of the components – *I*, obtained by fitting of CEMS spectrum collected for nitrided cast steel A

Sample A	*B* (T)	IS (mm/s)	QS (mm/s)	*I* (%)
	33.60(3)	0.22(1)	0.00	24
Fe_4Ni	21.45(2)	0.31(1)	0.20(1)	48
	21.53(3)	0.29(1)	–0.43(1)	24
Martensite	33.03(3)	–0.02(1)	0.00(1)	1
Other	0.00	0.33(1)	1.12(8)	3

examplarily in Table 4). The sextets strongly overlap with other components of the spectra, therefore, in order to evaluate the relative content of phases, a fixed ratio between intensities of the three sextets: 1:2:1 has been assumed. Percentage of subspectra corresponding to the individual phases is presented in Table 3. It is evidenced that the nitride γ'-Fe_4N predominates in the surface layer of samples A, B, C and intensity of the corresponding subspectrum reaches 82–96%. A little share of other components that can be attributed to ε-$Fe_{2\text{-}3}N$ or cementite has been also found. However, in the sample D the phase γ'-Fe_4N is absent and only small percentage of iron nitride (ε-$Fe_{2\text{-}3}N$) has been observed. Decrease of iron in martensite in favour of ferrite is also observed for this sample.

From CEMS spectra (for example, shown in Fig. 3a) collected after sequential rub of several layers, depth profile of the iron nitrides has been obtained using the same fitting procedure. The results are presented in Fig. 3b. It appears that the share of nitride γ'-Fe_4N diminishes rapidly with depth *d* of the layer under nitrided surface, while the concentration of ε-$Fe_{2\text{-}3}N$ at first slightly rises and then decreases. Total relative content of iron nitrides is reduced below 20% at $d = 0.015$ mm and is vestigial at 0.02 mm. These results are consistent with findings obtained by the use of a microscope that for the width of optically altered zone give the value: $0.015 \text{ mm} \le d \le 0.02$ mm. The analysis of results of microscopic investigations evidences that nitriding induces comminution and unification of the surface layer structure, independently of the chemical composition of cast steel [1].

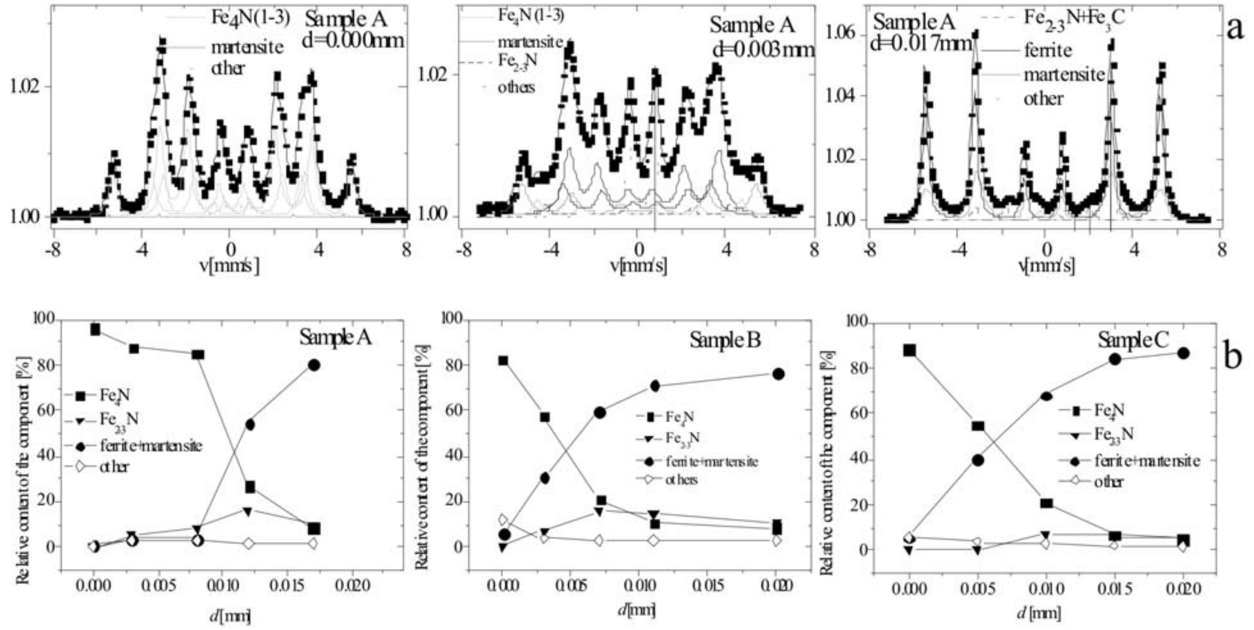

Fig. 3. Layer-to-layer analysis: Mössbauer spectra collected for sample A at the depth *d* under the nitrided surface (a) and distribution of iron over individual phases vs. *d* derived from CEMS spectra collected for cast steels A–C (b) (the absolute uncertainties are about 5%).

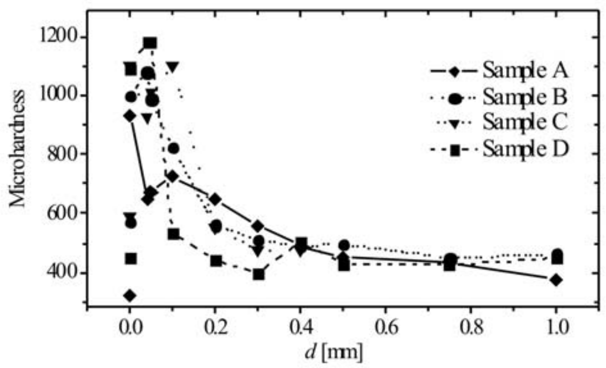

Fig. 4. Microhardness distribution in the cross-section of nitrided cast steels (*d*-depth under the nitrided surface). Single experimental points represent surface microhardness of as-cast samples. The relative uncertainties are about 5%. Evaluated dispersion originated from inhomogeneity of the material is equal to ±50.

Mechanical properties

In all the investigated cast steels, microhardness of the superficial region increased above twice after the nitriding procedure. The microhardness profile (shown in Fig. 4) exhibits a rapid drop at the depth about 0.1 mm and then it slowly declines up to the value characteristic of the as-cast material, which is reached at about 0.3 mm. These depth values are much larger than width of the surface layer comprising iron nitrides, derived from CEMS investigations. It suggests that the microhardness growth is caused not only by the presence of iron nitrides, but also by changes in microstructure and/or iron-less phases containing nitrogen, for instant carbonitrides. This presumption is confirmed by the results obtained for sample D: microhardness at the surface of this material increases after nitriding (similarly in other samples) while only very little amount of Fe_3N has been found there.

Friction tests evidence a significant increase of abrasion resistance after nitriding: intensity of abrasive wear (in the range of stabilized working) in all the investigated cast steels has been reduced by (40–60)%.

Conclusions

Both Mössbauer and XRD results show that the efficiency of nitriding of the cast steels with a similar carbon concentration strongly depends on chromium content and for 15 wt.% in the sample, which had been previously subjected to thermochemical treatment, only vestigial presence of iron-nitrogen phases is stated. Regarding other cast steels, the share of iron in the phase γ'-Fe_4N equals above 80%. This relative content decreases with depth under the nitrided surface. Simultaneously, a slight rise of the phase ε-$Fe_{2\text{-}3}N$ is observed. It was found on the basis of layer-to-layer CEMS analysis that the effective depth of the layer containing iron-nitrogen phases equals about $d = 0.015$ mm. This result is in accordance with findings of microscopic investigations that give the value: $0.015 \text{ mm} \leq d \leq 0.02$ mm.

It was stated that nitriding of cast steels causes about a 100% increase of microhardness and thickness of the zone characterized by enlarged hardness exceeds many times size of the layer comprising iron nitrides. Therefore, we can conclude that the observed increase of hardness of the investigated cast steels after nitriding is caused not only by the presence of iron-nitrogen phases, but also by other forms of nitrogen compounds as well as changes in microstructure of the surface zone.

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