The influence of surface layer nitriding on phase composition and tribological properties of cast steel

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Abstract. The effect of two-stage low-temperature nitriding on atomic structure and mechanical properties of selected cast steels is investigated. Conversion electron Mössbauer spectroscopy has been used to investigate nitrides formation. In order to study tribological characteristics, tests of friction and reflecting electron microscopy measurements have been performed. It has been found that thin nitrides layer (composed mainly of $\gamma$-Fe$_4$N) arises in the course of the nitriding procedure in most of investigated cast steels, what considerably affects their microstructure and tribological properties.

1. Introduction

Nitriding consists in saturation of the surface layer of metals or alloys with nitrogen during chemical and thermal treatment. It is known as method of improving some mechanical and chemical properties of the host material [1-3]. This is particularly important in case of cast steel, because of the possibility of inexpensive and precise production of metal details of machines and devices. In contrast to steel [3-8], there are not many reports related to properties of nitrided cast steel up to now [9-11]. In this paper, an influence of nitriding on phase composition and tribological properties of surface layer of highly-alloyed cast steel was examined. In order to study phase composition of the surface layer, conversion electron Mössbauer spectroscopy (CEMS) was used that yields information from the surface layer about 100 nm thick.

2. Experimental

Six kinds of highly-alloyed cast steel (denominated: A, ..., F) were investigated. The materials differed mainly in respect of chromium as well as carbon percentage. The concentration of alloying constituents of investigated cast steel samples is presented in Table I.

Two-stage low-temperature nitriding was performed in Institute of Precision Mechanics in Warsaw. In the first stage the cast steel was subjected to four hours long treatment in pure ammonia at 480°C, while in the second one the mixture of ammonia (40%) and previously dissociated ammonia (60%) was applied at 530°C during 16 hours. Mössbauer measurements were carried out in a backscattering geometry, using $^{57}$Co(Rh) source of gamma radiation and a gas-flow detector supplied with He+4%CH$_4$ mixture (for electron detection). CEMS spectra were numerically analyzed by means of NORMOS program. Investigations of abrasive wear resistance were realized according to the PN-
83/H-04302 Polish Standard, performing test of friction in system: three rollers - cone. Besides, tracks of wiping were analysed by means of reflecting electron microscope.

**Table 1.** Real concentration of alloying constituents (in weight %) in investigated cast steel samples; \( p \) means the total alloying percentage. The small amount of phosphorus (<0.03%) and sulphur (<0.015%) was neglected.

| sample | C    | Si   | Mn   | Ni   | Cr   | Mo  | V   | Cu  | \( p \) |
|--------|------|------|------|------|------|-----|-----|-----|--------|
| A      | 0.21 | 0.55 | 0.46 | 0.69 | 2.80 | 0.27| 0.27| 6.50 |
| B      | 0.64 | 0.48 | 0.54 | 0.75 | 2.63 | 0.23| 0.54| 1.22 | 6.40  |
| C      | 0.11 | 0.31 | 0.54 | 0.73 | 7.40 | 0.48| 0.25| 1.80 | 11.5  |
| D      | 0.70 | 0.37 | 0.39 | 0.68 | 7.49 | 0.43| 0.26| 1.90 | 11.5  |
| E      | 0.18 | 0.54 | 0.42 | 0.65 | 13.70| 0.76| 0.24| 1.58 | 17.9  |
| F      | 0.55 | 0.53 | 0.42 | 0.60 | 13.70| 0.35| 0.26| 1.82 | 17.7  |

3. Results

Mössbauer spectra collected before and after the nitriding process (Fig. 1) show significant changes in the phase structure of investigated specimens. While components characteristic of ferrite, martensite and (in a much smaller degree) austenite are mainly present in the spectra of the as-cast samples (Table 2), a significant contribution of subspectra attributed to iron nitrides has been found for most cast steels after nitriding.

![Figure 1](image-url)

**Figure 1.** Example Mössbauer spectra of selected samples (see Table I).

In iron – nitride system, \( \gamma^{-}\text{Fe}_4\text{N}, \varepsilon^{-}\text{Fe}_3\text{N}, \varepsilon^{-}\text{Fe}_3\text{x}\text{N} \) and \( \zeta^{-}\text{Fe}_2\text{N} \) are well known stable phases at room temperature. Unfortunately, their Mössbauer spectra, mostly composed of several Zeeman sextets, are strongly overlapped. Components related to other phases containing iron, for instance
carbon nitrides or carbides should be also taken into account. Therefore, in order to separate the phases credibly, fitting the spectra with some imposed restrictions was realized. Since it was found that γ-Fe₄N dominated among phases comprising nitrogen in most nitrided samples, the main constraint was a fixed intensities ratio (1:2:1) of three subspectra composing γ'-Fe₄N pattern – with magnetic hyperfine field values equal to about 34 T, 21.5 T, 21.9 T, isomer shift values (relative to pure iron) equal to 0.24 mm/s, 0.31 mm/s, 0.30 mm/s and quadrupole splitting values: 0, 0.19 mm/s, -0.39 mm/s, respectively. Assuming similar f-factor, the relative fraction of iron atoms contributed to individual phases was estimated.

**Table 2.** Relative fraction of iron atoms (in %) contributing to individual phases, estimated from Mössbauer spectra (a.c. – as cast samples, nitr. – nitrided samples)

| sample     | A | B | C | D | E | F |
|------------|---|---|---|---|---|---|
| martensite | 77 | - | 73 | - | 74 | - |
| ferrite    | 19 | 3 | 17 | 1 | 22 | 4 |
| austenite  | 2  | 2 | 6  | 2 | 2  | 2 |
| γ'-Fe₄N    | -  | 94| -  | 94| -  | 92|
| ε-Fe₂₋₃N  | -  | 1 | -  | 3 | -  | 2 |
| other      | 2  | - | 4  | - | 2  | - |

The results derived by means of numerical analysis of spectra obtained for as-cast specimens as well as for nitrided ones are collected in Table 2. The outcomes prove that applied nitriding procedure was very efficient in all cases apart from samples F and E, which show much smaller amount of iron-nitrogen phases. These samples are characterized by maximal content of chromium and specimen F – also relatively high carbon concentration, which probably prevents creating iron nitrides. In other samples, γ'-Fe₄N predominates in the surface layer. A small amount of phases ε is also present, which is probably the effect of oxidation of the perovskite γ'-Fe₄N phase towards the hexagonal one [12].

![Figure 2](image-url). Selected results of the test of friction in system: three rollers – cone (according to the PN-83/H-04302 Polish Standard). The blue lines and the red ones are related to the as-cast and nitrided specimens, respectively.
The results obtained by means of Mössbauer spectroscopy are well correlated with the outcomes of tribological examinations, presented in Figure 2a, b, c, d. Although it has been found that all investigated samples show enlarged abrasive wear resistance after nitriding, the value of this effect is different. The minimal reduction of depth of wiping (close to zero) is observed for sample F, the maximal for samples C, B, A. In sample D the relative improvement is only just of the order of 25%, but the abrasive wear resistance is good both before and after nitriding (the depth of wiping is of the order of 0.1–0.15 mm). Time evolution of wear suggests that nitrides layer is relatively thin.

The analysis of microscopic outcomes proves that in all the samples the nitriding procedure causes comminution and unification of surface layer structure, independently on the chemical composition of the cast steel.

4. Summary
An influence of nitriding on phase composition and tribological properties of surface layer of highly-alloyed cast steel was examined. The Mössbauer spectroscopy outcomes proved that low-temperature nitriding was efficient in all cases apart from the sample comprising maximal amount of chromium together with relatively high carbon concentration, which probably prevented creating iron nitrides. In other samples, \( \gamma' \)-Fe,N predominated in the surface layer. The results of tribological measurements (test of friction) evidenced enlarged abrasive wear resistance of the specimens submitted to the nitriding.

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