Nanoindentation study of layers after chemical–heat treatment of 27MnCrV4 steel

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Abstract. Nanoindentation testing is a method that consists essentially of touching the material of interest whose local mechanical properties as are hardness and elastic modulus are unknown. Nanoindentation testing is simply an indentation test in which the length scale of the penetration is measured in nanometres (10⁻⁹ m) rather than microns (10⁻⁶ m) or millimetres (10⁻³ m), the latter being common in conventional hardness tests. Both load and depth of penetration are recorded at each load increment (ultimately providing a measure of modulus and hardness as a function of depth beneath the surface). The method is most suitable for evaluating of mechanical properties of thin surface layer or particular microstructural constituents and phases. In this sense, there were evaluated nanoindentation hardness and Young modulus of some structural constituent on saturated layer after nitriding of the 27MnCrV4 cast high strength steel during the realized experiments.

1. Introduction

The quastistatic nanoindentation technique has been applied in the experimental tests of this presented article. Nanoindentation technique has been used in many engineering fields including biomedical, civil, mechanical and material engineering.

Authors Iracheta et al. [1,2] presented ccharacterization of material property variation across an inertia friction welded CrMoV steel component using the inverse analysis of nanoindentation data and also the influence of the indentation size and relation to the size of the microstructure of three polycrystalline materials indented with a Berkovich indenter.

Chen et al. [3] studied the effect of grain orientation on nanoindentation behaviour of model austenitic alloy Fe-20Cr-25Ni.

Authors Guo et al. [4] realized measurements of mechanical properties of micro constituents in Nb-Si-Ti alloy by micropillar compression and nanoindentation technique.

Recently, numerous analytical methods have been developed for characterization of basic mechanical properties (elastic modulus, yield stress, strain hardening exponents etc.) from the load penetration depth data of indentation tests. Unlike conventional tests, the indentation test allows determining the local material properties in the indented region. Due to this feature, indentation has been extensively used in characterizing mechanical properties in the microstructure of investigated material.

Nitriding layer obtained by saturation of steel surface by nitrogen consist of some sublayer and characteristic constituents which are also suitable to for observing by nanoindentation and evaluate its localised mechanical properties.
2. Basics of nitriding process
Nitriding is a heat treatment process that diffuses nitrogen into the surface of steels and cast irons to create a case-hardened surface. This diffusion process is based on the solubility of nitrogen in iron, as shown in the iron-nitrogen equilibrium diagram which can be seen in Figure 1.

![Iron-nitrogen equilibrium diagram](image)

Figure 1. Iron-nitrogen equilibrium diagram [5].

The solubility limit of nitrogen in iron is temperature dependent, and at 450 °C the iron-base alloy will absorb up to 5.7 to 6.1% of N. Beyond this, the surface phase formation on alloy steels tends to be predominantly epsilon (ε) phase (Fe₃N₁+ₓ). This is strongly influenced by the carbon content of the steel; the greater the carbon content, the more potential for the ε phase to form. As the temperature is further increased to the gamma prime (γ′) phase (Fe₄N₁₋ₓ) temperature (above 490 °C) limit of nitrogen solubility begins to decrease, therefore that temperature range is inappropriate for effective nitriding process. The equilibrium diagram shows that control of the nitrogen diffusion is critical to process success [5].

Authors Pokorný et al. [11] investigated the effect of nitrogen on surface morphology of layers. Common nitriding layer depth is from 0.05 to 0.5 millimetres. Schematic of a typical nitrided layer structure is in Figure 2. There can be very thin (1÷2 µm) oxide sublayer on the surface improving corrosion resistance and decreasing the friction. Next part is the compact nitride sublayer (white layer) with thickness about 5÷20 µm. White layer consists of ε phase mainly what gives it high hardness, protection against abrasive and adhesive wear and low friction coefficient. Final part and most important part of nitridic layer is a diffusion sublayer consisting iron (α″ – Fe₁₆N₂) as well as alloy nitrides (MeNₓ). Besides increased hardness, this subpart significantly improves fatigue properties [6].

![Schematic of a typical nitrided layer structure](image)

Figure 2. Schematic of a typical nitrided layer structure [5].
3. Experimental methods – quasisatic nanoindentation

The quasistatic nanoindentation tests involve pushing a diamond tipped indenter head into a material under either load or displacement control. The displacement \((h)\) is monitored as a function of the load \((P)\) throughout the load-unload cycle where resulting relation \(P-h\) is called nanoindentation curve. However, elastic – plastic contact occurs in real materials. There are both plastic and elastic deformations during indentation test on examined material surface. Once the forces are no longer applied, elastic part of deformation is recovered, where the plastic part remains in a form of indent (impress) on the material surface [7]. Plastic part of deformation is typically used to determine Young’s Modulus, while the elastic-plastic part both with indent surface is used to evaluate the hardness. The area bounded by both loading and unloading curves is equivalent to dissipation energy. Hardness \((H)\) is defined as the contact pressure under the indenter:

\[
H = \frac{P}{A_c}
\]

(1)

where \(P\) is the load and \(A_c\) is the projected contact area calculated at a depth of indentation \(h\). The initial slope \((S)\) of the unloading curve can be related to the elastic modulus of the material using equation:

\[
S = \frac{dP}{dh} = \frac{2E_r\sqrt{A_c}}{\sqrt{\pi}}
\]

(2)

where \(S\) is the initial slope of the unloading curve or contact stiffness, \(P\) is the applied load and \(E_r\) is the reduced modulus. As the measured displacement in a nanoindentation experiment is a combination of the displacement of the indenter tip as well as the specimen, the specimen modulus \((E_s)\) can be related to the reduced modulus \((E_r)\) using equation 3 provided the indenter modulus \((E_i)\) is known and the Poisson’s ratios of the specimen and indenter \((\nu_s\) and \(\nu_i\) respectively) are known or can be estimated:

\[
\frac{1}{E_r} = \frac{1-\nu_s^2}{E_s} + \frac{1-\nu_i^2}{E_i}
\]

(3)

When determining material properties such as hardness and elastic modulus a three-sided diamond pyramid indenter known as Berkovich indentation tip (can be seen in Figure 3 and Figure 4) is commonly used. According to some authors [8, 9] the diamond indenter behaves rigidly and equation 3 can be reduced to equation 4 by assuming \(E_i\). When determining material properties such as hardness and elastic modulus a three-sided diamond pyramid indenter known as Berkovich indentation tip (can be seen in Figure 4) is commonly used:

\[
\frac{1}{E_r} = \frac{1-\nu_s^2}{E_s}
\]

(4)

Figure 3. Overall view on the 3D model of Berkovich indentation tip, where \(\alpha = 65,25^\circ\) [10].

Figure 4. Real view on the Berkovich indent described through the SPM (Scanning Probe Microscopy) technology.
4. Experimental material
High strength middle alloyed cast steels G27MnCrV4 with are used for experiment (see Table 1). The experimental specimens are made by cast of the steel using investment casting process to the ceramic shell mould. Chemical composition of cast specimens was evaluated by spectral analyser SpectroLab Jr CCD. Measured concentrations of each element is shown in Table 1 where every value is average from minimally five measurements of the same sample. Basic mechanical properties (see Table 2) of the material were evaluated by standard testing procedures according to corresponding EN standards (Tensile strength test, Charpy impact test and Vicker’s hardness test).

Table 1. Chemical composition and basic mechanical properties of 27MnCrV4 steel.

| Element | C   | Mn  | Si  | Cr  | Mo  | Ni  | V   | Ti  | P   | S   |
|---------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| (wt. %) | 0.298 | 1.47 | 0.54 | 0.807 | 0.577 | 0.097 | 0.343 | 0.002 | 0.026 | 0.020 |

Table 2. Chemical composition and basic mechanical properties of 27MnCrV4 steel.

| Property | $R_m$ (MPa) | $R_{p0.2}$ (MPa) | A (%) | HV5 | KCU (J cm$^{-2}$) |
|----------|-------------|-----------------|------|-----|------------------|
|          | 1319        | 1173            | 4    | 543 | 11               |

In order to create suitable nitriding layer, the experimental samples were nitrided in gas nitrogen atmosphere with 85% NH$_3$ content at temperature $T=500$ °C and with holding period $t=2$ hours. The acquired microstructure of nitriding layer is depicted in Figure 5.

Figure 5. Microstructure of nitriding layer, mat. 27MnCrV4, $T=500$ °C, $t=2$ h, etch. Nital.

5. Experimental results
Targets of experiments are white compact nitride sublayer and the beginning of diffusion sublayer. Both these subparts of nitriding layer are relatively thin and therefore it is difficult to evaluate them by conventional testing methods as are hardness or micro hardness test. However, nanoindentation testing is very suitable to evaluate these parts of nitriding layer. Beside this, nanohardness or reduced Young modulus could be evaluated for specific part of the layer or particular phases and structural compounds with using of quasistatic nanoindentation. Device Triboindenter TI950 by Hysitron is used for experimental tests.
5.1. White layer investigation

White layer after nitriding with using of the parameters stated above is shown in Figure 6. It is compact but not uniform by thickness in range between 7−8 µm (Figure 6). The outer part of the compound layer is somewhat porous. The formation of porosity is due to the decomposition of thermodynamically unstable nitrides into iron and nitrogen gas at discontinuities (grain boundaries, slag inclusions, etc.). Presence of pores in compound layer has conflicting effects. In one view, pores result in poor adherence and low superficial hardness. In the other view, pores will form small reservoirs to hold surface lubricants to increase run-in and create a self-lubricating surface with higher wear resistance. Therefore, an optimum density of porosity in the compound layer would help to increase the wear resistance. Increasing in nitriding time and temperature leads to increasing in porosity.

![Figure 6. White layer after nitriding of mat. 27MnCrV4 and its thickness (µm) (T=500 °C, t=2 h, etch. Nital).](image)

![Figure 7. SPM image of white layer and location for indentation test (16x16 µm area).](image)

![Figure 8. 3D visualisation of SPM image of white layer (gradient).](image)

The SPM image of white layer and location where nanoindentation was performed, can be seen in Figure 7 and 3D visualisation of SPM data in Figure 8. SPM image shows two characteristic part of the white layer. A row of three nanoindentation tests is performed in both of them (can be seen in Figure 7). Another row of next three measurements is realized in the beginning of diffusion zone outside white layer for comparing with previous results. Measured values of nanohardness $H$ (GPa) is shown in Table 3 and values of reduced modulus $E_r$ (GPa) in Table 4.
Table 3. Experimental results of nanohardness $H$ (GPa) measured in white layer.

| Location | $H_1$  | $H_2$  | $H_3$  | Mean | St.dev. |
|----------|--------|--------|--------|------|---------|
| 0 ÷ 2    | 8.71   | 8.62   | 8.91   | 8.75 | ±0.15   |
| 3 ÷ 5    | 10.08  | 10.96  | 10.08  | 10.37| ±0.51   |
| 6 ÷ 8    | 4.82   | 5.72   | 4.20   | 4.92 | ±0.76   |

Table 4. Experimental results of reduced modulus $E_r$ (GPa) measured in white layer

| Location | $E_{r1}$ | $E_{r2}$ | $E_{r3}$ | Mean | St.dev. |
|----------|----------|----------|----------|------|---------|
| 0 ÷ 2    | 207.12   | 191.05   | 210.43   | 202.87| ±10.37 |
| 3 ÷ 5    | 158.76   | 164.65   | 160.96   | 161.45| ±2.98  |
| 6 ÷ 8    | 100.54   | 109.16   | 91.85    | 100.52| ±8.65  |

The values of nanohardness $H$ in upper part of the white layer (8.75±0.15) are relative lower in compare to values from bottom part (10.37±0.51). The values reflect the observation from microstructure study and SPM that upper part is mildly porous. Bottom part of the white layer is compact and consists of $\varepsilon$ phase mainly what leads to its higher hardness. Mixed hydrogen saturated microstructure below white layer has lower hardness in compare to hardness of the white layer (4.92±0.76). Course of reduced modulus $E_r$ values is different from hardness values. Highest values of $E_r$ were measured in the upper part of white layer. Epsilon phase has very high hardness and relatively lower plastic properties as a ferrous nitride what correspond with values of $E_r$ measured in bottom compact part of the white layer.

5.2. Course of nanohardness and reduced modulus through nitriding layer

Also course of nanohardness through visible part of nitriding layer and corresponding values of reduced modulus were measured. The results can be seen in Figure 9.

![Figure 9. Course of nanohardness and reduced modulus through nitriding layer.](image-url)
Principles of nanoindentation process allow to measure the hardness and reduced modulus from almost absolute top of the nitriding layer. The step between each other indentation place is chosen to 20 µm. It is difficult to realize such a little spacing with conventional microhardness testing. As expected, hardness values are decreasing exponentially from the highest hardness of the white layer to lowest values on the end of the hydrogen saturated layer. Beside this, the values of the reduced modulus are not so uniform and varying in dependency on the particular phase or structure compound where the each indent placed.

6. Conclusions
Nitriding layer after saturation of the steel surface by gas nitrogen has several characteristics parts and sublayers with different local mechanical properties as are nanohardness and reduced modulus. Highest values of nanohardness was measured in the part of white layer without porosity, consisting compact nitride – ε phase. Nanohardness decreases exponentially from maximal values in the white layer to lower values approaching hardness of base material. Reduced modulus varying in dependence to particular structure constituent. Based on this, the modulus could be used to mapping distribution of the phases present in the nitride layer. Investigated steel has complicated mixed microstructure due to relative high alloying element content. Therefore, more detailed phases as are nitride particles are not visible observing the steel with using the SPM microscopy built-in for used nanoindentor.

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