Influence of Chemical Composition on Layer Properties of Barrel Steels

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This article deals with influence of chemical composition on depth of diffusion layers and porosity of compound 
layers after gas nitriding process. Experiments are focused on utilizing of gas nitriding processes for surface treat-
ment. Gas nitriding technologies were applied to steels C 35 (sample A1), 34Cr4 (sample A2) and steel 42CrMo4 
(sample A4), which were subsequently evaluated by electron microscopy, GDOES and microhardness methods. 
The measurements showed the influences of chemical composition of alloying elements in core of material after 
chemical-heat treatment process on depth of diffusion and influence of technology on development of porosity. 
Nevertheless, the main task was the description of the porosity development in compound layer after gas nitriding 
and the increasing of surface hardness and of the depth of diffusion layer according to chemical composition. Gas 
nitriding process was applied for increasing of surface hardness of material in depth and improving of mechanical 
properties. Mechanical properties of tested material were significantly increased.

Keywords: gas nitriding; microhardness; nitrided layer; porosity.

1 Introduction

Non-equilibrium structure is due to redistribution of 
alloying elements in crystal lattice more suitable for dif-
fusion process. The aim of this paper is to achieve an en-
hanced surface hardness and reduced friction coefficient 
with predictable occurrence of porosity. It is well known 
that the nitrides of iron are primarily created during the 
nitriding process. These types of nitrides caused only lit-
tle increasing of microhardness level. The alloying ele-
ments, such as Cr, Mo, ensure faster and higher increas-
ing of mechanical properties. Their impact to the creation 
of diffusion layer is described in this paper. During gas 
nitriding process, two different layers are mostly effec-
tively created. Firtly, a compound layer which is con-
sisted of ε-Fe₂₋₃N and γ-Fe₄N phase is usually created on 
the surface of steel [1, 2]. Ratio of individual phases is 
dependent on the carbon concentration in steel [1]. 
The compound layer has been very hard and brittle with good 
friction and anticorrosion properties [2]. Secondly, a dif-
fusion layer which are mostly created underneath the 
compound layer.

After the finish of gas nitriding process a new estab-
lished compound layer mostly contents pores, for instead 
the significant occurrence of pores very often exists in the 
surface and defined depth of compound layers. There are 
many options which are able to be used to pores. The 
thickness and hardness of γ′-Fe₄N (diffusion layer) de-
pends on quantity and quality of alloying elements [3-5]. 
This article describes the influence of selected alloying 
elements on the thickness of the diffusion layer and on the 
porosity of the compound layer. The porosity is always 
presented in the surface layer and be able to have bad in-
fluence on mechanical properties and the wear resistance.

Chemical composition of steel was checked up by 
GDOES/Bulk method on LECO SA 2000 spectrometer 
and local measurement of composition was carried out on 
SEM microscope Hitachi Tabletop 3000. Microstructure 
was evaluated by electron microscopy method on Hitachi 
Tabletop 3000. Thickness and microhardness of nitrided 
layers were measured by microhardness method in ac-
cordance with DIN 50190 standard on automatic micro-
hardness tester LECO LM 247 AT [6, 7].

2 Materials and methods

Steel C35 (sample A1), 34Cr4 (sample A2) and 
42CrMo4 (sample A4) in untreated state were heat-
treated (Tab. 1). The quenching and tempering processes 
were performed due to obtain two different microstruc-
tures with different parameters of initial microhardness 
and different redistribution of ion in crystal lattice.

Tab. 1 Temperatures of heat-treated steels

| Steel  | Sample | Procedure |
|--------|--------|-----------|
| C35 A1 | 860 °C, water  | 600 °C, air |
| 34Cr4 A2 | 840 °C, water | 600 °C, water |
| 42CrMo4 A4 | 850 °C, oil  | 600 °C, water |

The chemical composition of material was evaluated by 
GDOES/Bulk method (Tab. 2). Glow discharge optical 
spectroscopy (GDOES) measurements were per-
formed in LECO SA-2000, with argon glow discharge 
plasma excitation source, calibration of nitrogen: JK41- 
1N and NSC4A standards.

Tab. 2 Chemical composition of A1, A2 and A4 steel measured by GDOES/BULK method

| Concentration [wt. %] |
|----------------------|
| Sample  | C  | Mn  | Si  | Cr  | Ni  | Mo  | Al   |
| A1      | 0.36 | 0.68 | 0.33 | 0.08 | 0.04 | -   | 0.003 |
| A2      | 0.35 | 0.70 | 0.35 | 1.06 | 0.05 | -   | 0.035 |
| A4      | 0.38 | 0.81 | 0.35 | 1.09 | 0.06 | 0.19| 0.019 |
The microstructure of samples was observed by utilizing electron microscopy method and was performed on SEM Hitachi Tabletop 3000 before and after chemical heat-treatment due to comparison of results. The structure after quenching is displayed in Fig. 1. The conditions of heat-treatment process are given in Tab. 1. Gas nitriding process was performed in NITREX appliance for 6 hours in two step process at 530 °C.

**Fig. 1 The chemically etched SE cross-sectional structure of tempered steel, magnification 2000x**

The microhardness of mentioned samples was evaluated by Vickers microhardness method on the automatic microhardness tester LM 247 AT LECO. Load set at 50 g and 10 s dwell time. This method was used for comparison of initial surface microhardness before and after chemical-heat treatment process. The measurements of initial microhardness of heat-treated samples are displayed in Tab. 3.

**Tab. 3 Initial microhardness of core of steel after heat-treatment**

| Steel   | Sample | Initial surface microhardness HV 0.05 | Quenched | Tempered |
|---------|--------|--------------------------------------|----------|----------|
| C35     | A1     | 499 ± 31                             | 266 ± 6  |
| 34Cr4   | A2     | 660 ± 29                             | 328 ± 11 |
| 42CrMo4 | A4     | 645 ± 24                             | 335 ± 22 |

**Fig. 2 The chemically etched SE cross-sectional structure of tempered steel A2, the measurement of thickness of compound layer, magnification 5000x**

After preparation and nital etching, the electron microscope Hitachi Tabletop 3000 was used for observation of thickness of compound layer (Fig. 2) and especially the documentation of porosity present in the top of compound layer (Fig. 3a-b). The porosity was measured by using SE method and magnification 5000x (Fig. 3), for detailing description the magnification 10000x was ensured (Fig. 6).

**Fig. 3a The chemically etched SE cross-sectional structure of tempered steel A1, compound layer with porosity (top of surface) and diffusion layer below, magnification 5000x**

**Fig. 3b The chemically etched SE cross-sectional structure of tempered steel A2, compound layer with porosity (top of surface) and diffusion layer below, magnification 5000x**

3 Results and discussion

The microstructure was evaluated by SEM method on microscope Hitachi Tabletop 3000. The structure was obtained by nital etching and was estimated as martensitic microstructure with marks of bainite (see Fig. 1). The chemical composition of steel was evaluated and checked by GDOES method on SA 2000 Leco surface analyzer. The measurements showed the specific chemical composition of selected steels, esp. chromium and molybdenum concentration (Tab. 2). The concentration of molybdenum and chromium influences the fundamental mechanical properties, esp. surface microhardness after chemical heat treatment processes (compare Tab. 2, Fig. 4). The experiments proved the importance of alloying elements concentration as Cr and Mo, and their influence
on the depth development. Moreover, the presence of these alloying elements caused the increasing of surface microhardness after chemical-heat treatment (Fig. 4).

It was proved that in case of sample A2, the surface hardness and the depth of diffusion after the chemical-heat treatment was getting up steeper than in case of sample A1. It was caused due to concentration of chromium in case of A2 sample. The concentration of alloying elements Mn, Si and interstitial element C is similar (see Tab. 2). The same trend of microhardness was confirmed in case of sample A4 (Tab. 2). Thanks to the same conditions of gas nitriding process there was possible to evaluate the influence of substitution elements on creation of surface hardness of diffusion layer and depth of nitriding (thickness of diffusion layer). The same progress is expected in case of concentration of V or Mo.

The depth of diffusion layer was increased by higher concentration of Cr and Mo (Fig. 4). By increasing of Ni concentration the hardness was decreased. This has to do with ability of Ni to create a nitrides or carbides.

Moreover, the experiments proved that the increasing of surface microhardness after gas nitriding process is depended on initial microhardness, better said on initial microstructure. This phenomenon was found out thanks to differences in microstructure after heat treatment process, esp. due to initial surface hardness before nitriding (compare Tab. 3, Fig. 5). The initial microhardness of steel after quenching is usually decreased during process of chemical-heat treatment to tempered values (see Fig. 5). The values of surface microhardness of diffusion layer was evaluated by microhardness method and was measured as a higher in case of quenched samples (Fig. 5).

In fact, the initial microhardness after quenching (Tab. 3) was decreased during the process of chemical-heat treatment due to high temperature close to the A1 curve in Fe-Fe₃C diagram. Regardless, there was reached higher values of surface microhardness after quenching than after tempering (Fig. 5). The reason is the different type of redistribution of ions in crystal lattice.

The thickness of compound layer was evaluated by SEM method on electron microscope Hitachi Tabletop 3000 and all results are given in Tab. 4. The lowest thickness of compound layer was measured on A1 sample but the differences of all measured thicknesses are very close. There is possible to consider as the same.

The porosity of compound layer was evaluated by using electron microscopy, too (Fig. 6). The size of pores was measured on electron microscope by magnification 10000x and the results are displayed in Tab. 4.
Tab. 4 Parameters of nitrided layers

| Sample | Compound layer thickness [µm] | Depth of diffusion layer [mm] | Porosity [nm] |
|--------|------------------------------|-------------------------------|---------------|
| A1     | 9.2                          | 0.02                          | 370-610       |
| A2     | 9.7                          | 0.20                          | 280-890       |
| A4     | 10.2                         | 0.19                          | 390-970       |

The influence of chemical composition on the sizes of pores was not confirmed. Porosity was present only in the top part of compound layer. The pores are created just only in new established part of compound layer.

Fig. 6 The chemically etched SE cross-sectional structure of tempered steel A4, documentation of porosity, magnification 10000x

This thickness of new established part of compound layer is similar to the dimensional accuracy after gas nitriding technology.

4 Conclusions

These evaluated steels with different chemical composition were used for experiments concerning the porosity, microhardness and thickness of compound layer. The basic steel C35 is not entirely suitable for application of diffusion processes due to non-effective increasing of mechanical properties (Fig. 4), what it has to do with chemical composition of steel, esp. the concentration of alloying elements which support the diffusion process inside. The alloying elements Mo and Cr was causing the increasing of surface microhardness and these elements have remarkable influence on microhardness and depth of diffusion layer. The influence of these elements to the thickness of compound layer was not confirmed. The most occurrence of pores was estimated in the top part of compound layer in all tested steels. The main area of occurrence of pores was established in part of new grown part of compound layer. We are able to reliably define this porosity layer as a new established layer having strict influence on dimensional accuracy. The significant result is a claim that the chemical composition of steel has no influence on occurrence of porosity. The proportions of pores (porosity) are dependent on selected technologies of chemical-heat treatment, it is not more about concentration of alloying elements. In many industry applications there is suitable to remove this part of layer due to creation of defects on the surface, esp. in case of barrels or gears. But in many cases there are new options to use this pores for storage of lubrication [1].

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References

[1] CLARKE, A., JAMALI, HU., SHARIF, KJ., EVAN, HP., FRAZER, R., SHAW, B. (2017). Effects of profile errors on lubrication performance of helical gears. In: Tribology International, Vol. 111, pp 184 – 191.
[2] KOSTUREK, R., NAJWER, M., NIESLONY, P., WACHOWSKI, M. (2018). Effect of Heat Treatment on Mechanical Properties of Inconel 625/Steel P355NH Bimetal Clad Plate Manufactured by Explosive Welding. In: Advances in Manufacturing, pp 681-686.
[3] DUBOVSKA, R., MAJERIK, J., BASKA, I., JAMBOR, J (2015). Investigation of cutting temperature during AlCu3MgMnPb aluminium alloy turning. In: Manufacturing Technology, Vol. 15, No. 5, pp. 796 – 801.
[4] HUTSAYLYUK, V., SIEZKE, I., CHAUSOV, M., TORZEWSKI, J., PYLYPENKO, A., WACHOWSKI, M. (2016). Cyclic deformation of aluminium alloys after the preliminary combined loading. In: Engineering Failure Analysis, Vol. 69, pp. 66 – 67.
[5] DOBROCKY, D., KUSMIC, D (2015). The Effect of Plasma Nitriding Process on the Change of Dynamic Parameters of Steel DIN 1654/4. In: Manufacturing Technology, Vol. 15, No. 1, pp. 14 – 20.
[6] ČSN ISO 14577-1 METALIC MATERIALS – Instrumented indentation test for hardness and materials parameters – Part 1: Test method.
[7] DIN 50190-4:1999, Hardness depth of heat-treated parts – Part 4: Determination of the diffusion hardening depth and the diffusion depth.

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