

CHARACTERIZATION OF GAS-NITRIDED 31CrMoV9 STEEL

KARAKTERIZACIJA PLINSKO NITRIRANEGA JEKLA 31CrMoV9

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In this work, gas nitriding of 31CrMoV9 was carried out at three different temperatures, i.e., at (500, 520 and 540) °C for (10, 20 and 30) h. The microstructure of the nitrided layer was examined with light and scanning electron microscopes. Depending on the process temperature and time, the thickness of the compound layer ranged from 8.7 μm to 22.7 μm. The γ' -Fe₄N, ϵ -Fe₃N and Cr₂N phases formed in the compound layer were determined with the XRD technique. It was found that the hardness of diffusion layer changed from 620 HV to 750 HV. The maximum surface hardness was determined as 920 HV. Depending on the process parameters, the case depth of diffusion layer ranged from 187 μm to 450 μm. Diffusion-coefficient and activation-energy values for the diffusion of nitrogen in the 31CrMoV9 steel were evaluated using studies on the kinetics of the growth of the nitrided layer. The activation energy of the nitriding process of the 31CrMoV9 steel is 150 kJ/mol.

Keywords: gas nitriding, kinetics, nitriding potential, nitride

Izvršeno je bilo plinsko nitiranje jekla 31CrMoV9 pri treh temperaturah (500, 520 in 540) °C v trajanju (10, 20 in 30) h. Mikrostruktura nitrirane plasti je bila preiskana s svetlobnim in elektronskim mikroskopom. Odvisno od temperature in trajanja procesa je bila debelina spojinske plasti od 8,7 μm do 22,7 μm. XRD-analiza je pokazala, da so v spojinski plasti nastale faze γ' -Fe₄N, ϵ -Fe₃N in Cr₂N. Izmerjena trdota difuzijske plasti se je spremenila od 620 HV na 750 HV. Maksimalna trdota površine je bila 920 HV. Odvisno od procesnih parametrov se je spreminjala debelina difuzijske plasti od 187 μm do 450 μm. Koefficient difuzije in vrednosti aktivacijske energije za difuzijo dušika v jeklu 31CrMoV9 so bile določene na osnovi študija kinetike rasti nitrirane plasti. Aktivacijska energija procesa nitiranja jekla 31CrMoV9 je bila 150 kJ/mol.

Ključne besede: plinsko nitiranje, kinetika, potencial nitiranja, nitrid

1 INTRODUCTION

Gas nitriding is a case-hardening process whereby nitrogen is introduced into the surface of a solid ferrous alloy by holding a metal at a suitable temperature (below A_{c1} for ferritic steels) in contact with a nitrogenous gas, usually ammonia. Quenching is not required for the production of a hard case. The nitriding temperature for all steels is between 495 °C and 565 °C. Because of the absence of a quenching requirement, with the attendant volume changes and the comparatively low temperatures employed in this process, nitriding of steels produces less distortion and deformation than conventional hardening¹. The formation of a nitrided layer, which improves the wear resistance of steel, proceeds in several stages. It starts at the moment of saturation of a matrix with nitrogen. On such an area the nucleation of nitrides can take place. A further development of the layer proceeds through the growth of these nuclei until a connection is made². By nitriding Fe–Me binary alloys, where the alloying element (Me) has a strong affinity with nitrogen, i.e., Me = Cr, Al, V and Ti, nanosized nitride precipitates can develop in the ferrite matrix; the nitride precipitation results in a very pronounced increase in the hardness³ because of the formation of nitrides that are stable at nitriding temperatures. Molybdenum, in addition to its contribution as a nitride former, also reduces the risk of embrittlement at nitriding temperatures¹. The modern, controlled, gas-nitriding process

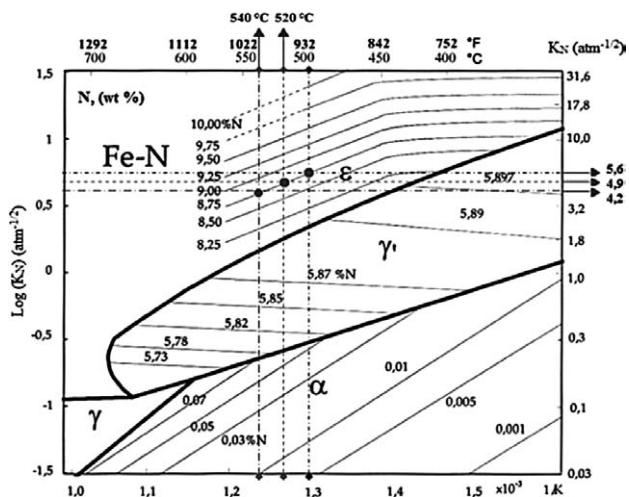
employs pure ammonia or ammonia with one or two additive gases and it is controlled not with the dissociation rate but with the nitriding potential, KN. Controlling the process with the thermodynamic parameter, KN, makes it possible to produce hardened layers that have variable metallurgical properties⁴. In the present work, the feasibility of nitriding the 31CrMoV9 steel through gas nitriding in an automatic KN-controlled Nitrex NX-412 model gas-nitriding furnace was investigated. The diffusion coefficient and activation-energy values for the diffusion of nitrogen in the 31CrMoV9 steel matrix were evaluated using studies on the kinetics of the growth of the nitrided layer.

2 EXPERIMENTAL DETAILS

A series of experiments was carried out to investigate the gas-nitriding response of the 31CrMoV9 steel. The chemical composition of the test material is given in **Table 1**. Specimens had a rectangular shape and the dimensions of 10 mm × 15 mm × 25 mm. The surfaces of the substrates were mechanically ground with the 100, 320, 400 and 600 grit SiC papers. Prior to the gas-nitriding treatment, the 31CrMoV9 steel samples were austenitized at 900 °C and tempered at 630 °C. The parameters for the experimental studies were selected according to the Lehrer diagram⁵ given in **Figure 1**. This diagram shows the areas of nitride phases and the lines of equal nitrogen concentrations.

Table 1: Chemical composition of nitrided 31CrMoV9 steel (w%)**Tabela 1:** Kemijska sestava nitriranega jekla 31CrMoV9 (w%)

C	Cr	Ni	Mo	V	Mn	Si	Al	Cu	Co	P	S
0.32	2.6	0.2	0.2	0.2	0.6	0.25	0.01	0.06	0.04	0.006	0.001

**Figure 1:** Presentation of gas-nitriding parameters on the Lehrer diagram⁵**Slika 1:** Predstavitev parametrov plinskega nitriranja na Lehrerjevem diagramu⁵

According to the Lehrer diagram,⁵ the values of the KN nitriding potentials were selected as (4.2, 4.9 and 5.6) $\text{bar}^{-1/2}$, providing the same nitrogen concentration on the surface at the selected temperatures (**Figure 1**). After the nitriding processes, a conventional microstructural examination was made on the ground and polished samples using a light microscope. A more detailed investigation of the metallographic structures was carried out using a JEOL JSM-5600 model scanning electron microscope (SEM).

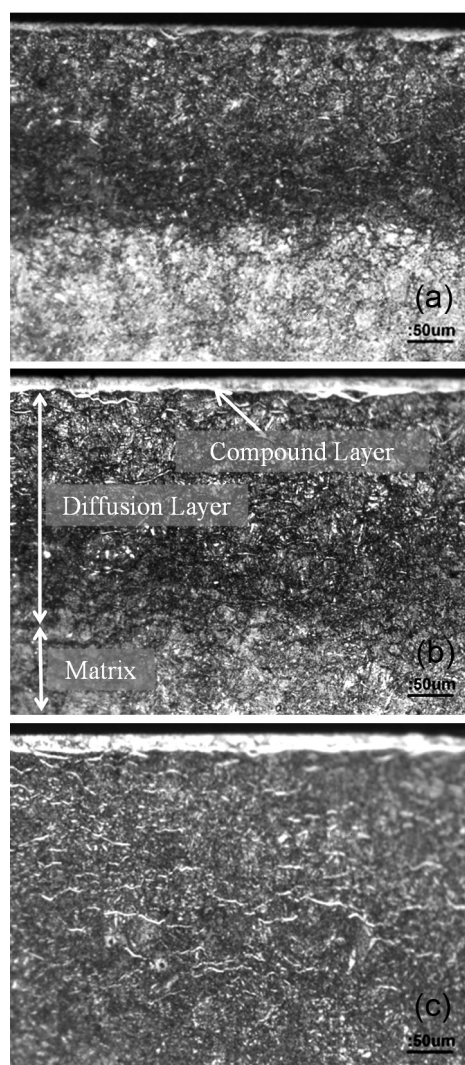
The hardness profile of the nitrided case was determined using a Leica WMHT-Mod model microhardness tester with a 0.98 N load in terms of HV, and the effective case depth was defined as the distance below the surface, where the hardness was equal to 350 HV. The phases, formed on the surfaces of the nitrided specimens, were identified with a Rigaku X-ray diffractometer using the $\text{Cu } K_{\alpha}$ radiation with a wavelength of 0.15418 nm over a 2θ range of 10° to 90° .

3 RESULTS AND DISCUSSION

Light microscopy examinations revealed that there are three distinct layers on the cross-section of a nitride sample; i) the fine external compound layer of nitrides, ii) the internal diffusion layer and iii) the matrix (**Figure 2**). The compound layer is formed on the top of the diffusion zone where dense and fine precipitates of iron nitrides are present and it preferentially grows in the whisker form through the grain boundaries (**Figure 3**).

The thickness and the composition of a surface layer that develops during the nitriding process are affected by the type of the chemical reactions occurring at the sample surface, the diffusivity of nitrogen in the treated material, the gas-mixture ratio, the process temperature, and the time⁶. The XRD pattern of the 31CrMoV9 steel nitrided at 540 °C for 30 h is given in **Figure 4**. By selecting the proper nitriding potentials in the ϵ -phase region according to the Lehrer diagram, the surfaces with a white layer consisting of two phases, the ϵ - Fe_3N and γ' - Fe_4N nitrides were obtained.

The values of the compound-layer thickness, the case depth and the surface hardness of the steel depending on

**Figure 2:** Microstructure of 31CrMoV9 steel nitrided at: a) 500 °C, b) 520 °C and c) 540 °C for 30 h**Slika 2:** Mikrostruktura jekla 31CrMoV9 nitriranega 30 h pri: a) 500 °C, b) 520 °C in c) 540 °C

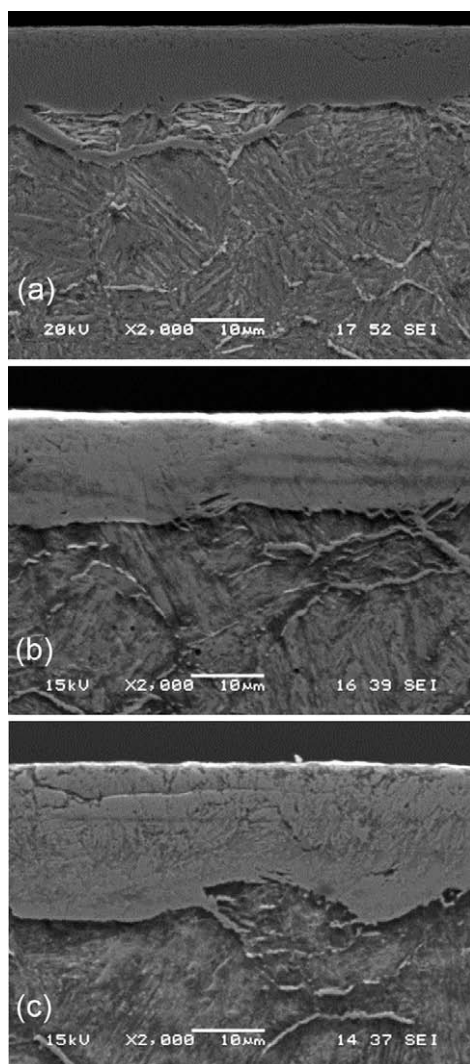


Figure 3: SEM micrographs of 31CrMoV9 steel nitrided at 520 °C for a) 10 h, b) 20 h and c) 30 h

Slika 3: SEM-posnetki jekla 31CrMoV9, nitriranega pri 520 °C: a) 10 h, b) 20 h in c) 30 h

the nitriding conditions are presented in **Table 2**. The hardness profiles for the nitriding samples as a function of the case depth are given in **Figure 5** for different

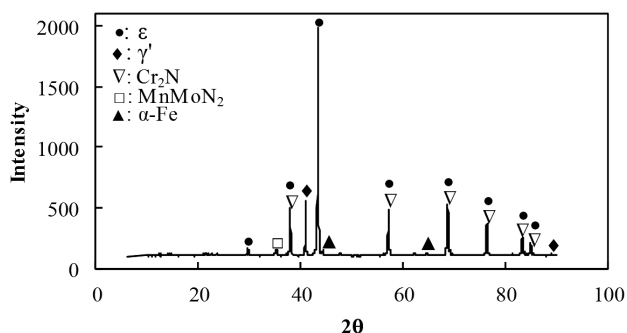


Figure 4: XRD pattern of 31CrMoV9 steel nitrided at 540 °C for 30 h
Slika 4: Rentgenski posnetek jekla 31CrMoV9, nitriranega 30 h pri 540 °C

nitriding conditions. The hardness of the nitride layer is much higher than that of the matrix due to the formation of hard Fe_4N , Fe_3N and Cr_2N nitrides in the compound layer as determined with the XRD analysis. At all the nitriding temperatures and times, the hardness continuously decreases from the surface to the core due to the decreasing nitrogen concentration. The maximum surface hardness, 920 HV, was obtained for the nitriding time of 10 h at 500 °C. The surface-hardness values decrease due to the increasing process temperature and time. The decrease in the surface hardness seems to be mainly associated with the white-layer thickness. As the increase in the white-layer thickness makes the compound layer more brittle, the surface hardness decrease is also due to the brittleness increase.

Table 2: Variation of the compound-layer thickness, case depth, diffusion coefficient of the case layer and surface hardness with the nitriding temperature and time

Tabela 2: Spreminjanje debeline spojinske plasti, globine nitriranja, difuzijskega koeficienta nitrirane plasti in trdote površine s temperaturo in trajanjem nitriranja

Nitriding temperature (°C)	Time (h)	Compound layer thickness (μm)	Case depth (μm)	Diffusion coefficient (10^{-8} (cm ² /s))	Surface hardness (HV)
500	10	8.70	210	0.614	920
	20	14.8	250		908
	30	17.1	350		870
520	10	12.8	230	1.153	914
	20	17.4	320		895
	30	20.4	370		860
540	10	17.0	250	1.94	910
	20	20.6	350		891
	30	22.7	450		821

As it can be seen from **Table 2**, the compound-layer thickness and the case depth increased with the increasing nitriding temperature and time (**Figures 2** and **3**). An increased time provides more atomic nitrogen diffusion towards the core while the increasing temperature raises the diffusion coefficient of nitrogen, providing the same effect. The solid-state diffusion of atomic nitrogen into the α -Fe matrix is assumed to obey Fick's second law. The growth of the nitrided layer is a consequence of the nitrogen diffusion perpendicular to the sample surface⁷. The layer growth kinetics is enhanced when increasing the surface nitrogen concentration. This effect is more pronounced with a rise in the temperature since the process becomes more active.

Primarily, diffusion-coefficient values were calculated using the $d^2 = Dt$ equation, where d is the case depth (μm), t is the process time (s) and D is the diffusion coefficient (cm²/s). The variation in the square of the case depth (d) as a function of the nitriding time is shown in **Figure 6a** for each temperature. The calculated diffusion-coefficient values are given in **Table 2**. To obtain the activation energy Q , connected to the effective diffusion coefficients, the Arrhenius plots, $\ln D$ versus

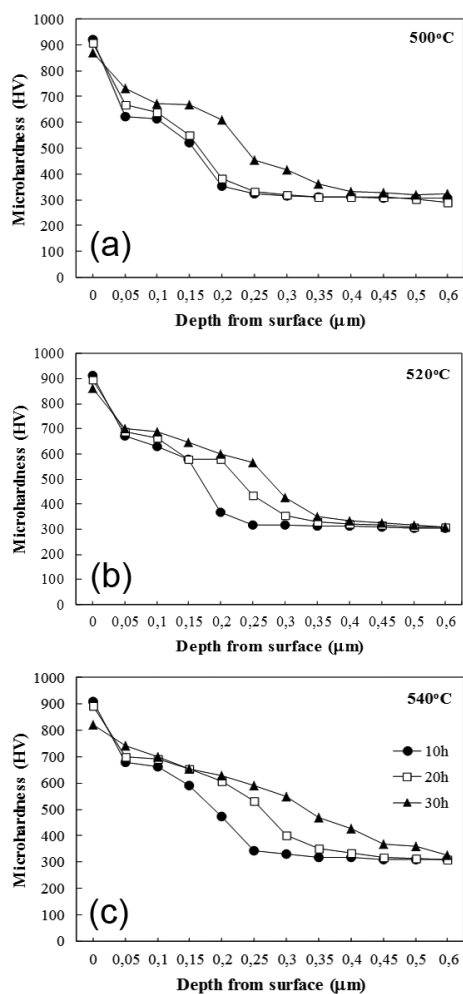


Figure 5: Microhardness profiles for the nitrided 31CrMoV9 steel at: a) 500 °C, b) 520 °C and c) 540 °C

Slika 5: Profil mikrotrdote nitiranega jekla 31CrMoV9 pri različnem trajanju nitiranja pri: a) 500 °C, b) 520 °C in c) 540 °C

$1/T$ are shown in **Figure 6b** for the nitriding temperature. The activation energy for the gas-nitrided 31CrMoV9 steel was found to be 150.48 kJ/mol. This is in reasonable agreement with the values in the other investigations^{8,9}.

4 CONCLUSIONS

In this work, the effect of the nitriding temperature and time on the development of the compound layers during the KN controlled gas nitriding of the 31CrMoV9 steel was investigated. It was found that the process parameters of gas nitriding considerably affect the diffusion-layer hardness and diffusion-zone thickness of a workpiece. They increased with the increasing nitriding temperature and time. The XRD analysis confirmed the presence of the γ' -Fe₄N and ϵ -Fe₃N phases. The kinetic study showed that the effective diffusion coefficient for the nitrided 31CrMoV9 steel depends

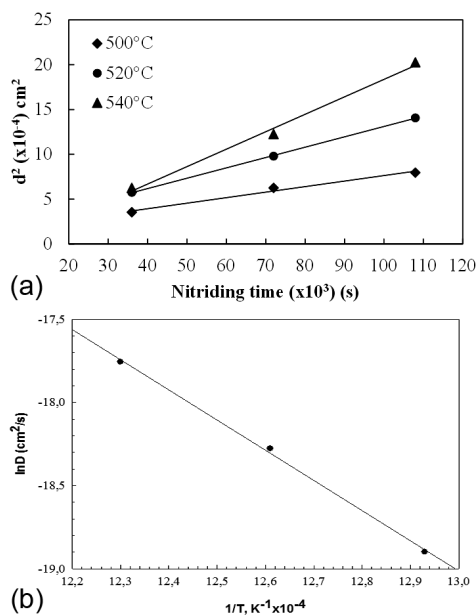


Figure 6: a) Variation in the square of the case depth as a function of nitriding time, b) change in the effective diffusion coefficient with the inverse of the process temperature

Slika 6: a) Spreminjanje kvadrata debeline nitiranja v odvisnosti od trajanja nitiranja, b) spreminjanje efektivnega koeficienta difuzije z obratno vrednostjo temperature procesa

considerably on the process temperature, and the diffusion coefficient increased with the increasing temperature. The activation energy of nitriding of the 31CrMoV9 steel was found to be 150 kJ/mol.

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