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MICROSTRUCTURAL FEATURES OF Cr-V LEDEBURITIC STEEL SATURATED WITH NITROGEN

ZNAČILOSTNI MIKROSTRUKTURE LEDEBURITNEGA JEKLA Cr-V, NASIČENEGA Z DUŠIKOM

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This paper reports on the microstructure, the hardness and microhardness, the nitrogen-concentration depth profiles and the phase constitution of plasma-nitrided P/M VANADIS 6 cold-worked steel. The initial microstructure of the steel consists of a matrix with twinned and dislocated martensite and particles of the carbides, MC and M_7C_3. After plasma nitriding the surface hardness and microhardness increased as a result of the nitrogen that diffused into the near-surface region. During the first stage the martensite is saturated with nitrogen, and after the solid-solubility limit is exceeded, nitrides like Fe_4N and Fe_3N are formed.

Key words: P/M cold-worked steel, plasma nitriding, twinned and dislocated martensite, phase constitution

Jeklo P/M VANADIS 6 za delo v hladnem je bilo nitrirano v plazmi. Preiskovane so bile pomembne lastnosti površine, kot so mikrostruktura, trdota in mikrotrdota, profil koncentracije dušika ob površini in sestava faz. Pred nitriranjem v plazmi je bila matrica iz dvojčičnega in dislokacijskega martezita in iz karbidov MC in M_7C_3. Po nitriranji se je povečala trdota in mikrotrdota površine zaradi difuzije dušika, ki se je najprej bogatil v martenzitu. Po preseženi topnosti pa so nastale nitridne faze Fe_4N in Fe_3N.

Ključne besede: P/M-jeklo za delo v hladnem, nitriranje v plazmi, dvojčični in dislokacijski martenzit, sestava faz

1 INTRODUCTION

Steels based on the quaternary Fe–C–Cr–V system are regarded as promising tool materials [1]. Because of their high alloying-element content they are mostly produced using powder-metallurgy techniques, which makes it possible to achieve an excellent combination of microstructure and mechanical properties. The Vanadis 6 steel, developed at Uddeholm AB, is a typical example of this type of steel [2]; it has good hardenability, an easily achievable hardness of 60 HRC, a high resistance to plastic deformation and a good combination of adhesive/abrasive wear resistance. On the other hand, the steel has low machinability and grindability because it contains a relatively large amount of hard carbide particles. The Vanadis 6 steel is a good substrate for plasma nitriding and/or surface coating.

Plasma nitriding is now well established as a surface-strengthening method for ledeburitic tool steels. The processing is carried out below the tempering temperature, which means that the microstructure and mechanical properties remain virtually unaffected. Since the low processing temperature does not induce a phase transformation in the matrix, the process is distortion free and the tools or the machine elements can be net-shape finished before the nitriding. The introduction of nitrogen atoms into the surface leads to the formation of compressive stresses in the nitrided region and to a beneficial effect on some of the mechanical properties. The characteristics of the nitrided region are very closely related to certain processing parameters and are controlled by regulating the gas flow, the temperature and the dwell time.

Most experimental investigations aimed at understanding the behaviour of steel during plasma nitriding were performed with conventionally produced or P/M M2–grade high-speed steel [3-5]. This makes sense because this type of steel is the one most widely used in the tool industry. Furthermore, the nitriding behaviour of this type of material is now relatively well understood. On the other hand, there is a lack of theoretical and practical experience when it comes to the nitriding behaviour of other P/M ledeburitic steels. For this reason we have focused on analysing the nitriding behaviour of the Cr-V ledeburitic steel Vanadis 6.

2 EXPERIMENTAL PROCEDURE

For the experimental work we used the P/M Vanadis 6 ledeburitic-type steel (2.1 % C, 7 % Cr, 6 % V, Fe bal.). All the specimens were net-shape machined, polished and heat treated to a hardness of 60 HRC. The plasma nitriding was carried out with RUBIG Micropuls – Plasmatechnik equipment using cracked ammonia without the addition of nitrogen and/or hydrogen.

General microstructural examinations involved the use of optical microscopy and scanning electron microscopy, whereas transmission electron microscopy was used to gather information about the phase constitution in the nitrided region. Thin foils were prepared using ion bombardment of small pieces cut from the nitrided specimens. In addition, collodion extract replicas were also prepared to allow us to identify the nitrides precipitated from the solid solution. The phase constitution was also investigated with X-ray diffraction. The Vickers surface hardness and microhardness were determined using a load of 10 kg (*HV* 10) for the surface hardness and a load of 50 g (*HV* 0.05) for the depth profiles. The depth profiles of the interstitials were established with a CAMEBAX microprobe analyser.

3 RESULTS AND DISCUSSION

The SEM micrograph in **Figure 1** shows that the microstructure of the substrate material consists of a matrix with fine, uniformly distributed carbide particles of regular, spherical shape, and with a size of several microns. The matrix consists of needle-like tempered martensite. A detailed examination revealed two basic types of martensite: the dislocated type, (**Figure 2**) typified by a high density of dislocations, and the twinned-martensite type (**Figure 3**).

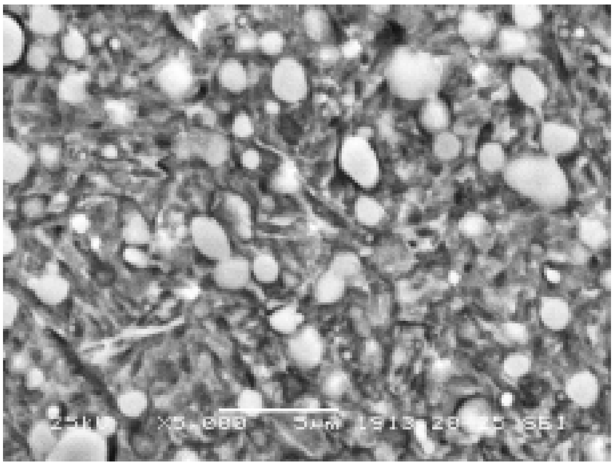


Figure 1: SEM micrograph of the substrate material
Slika 1: SEM-posnetek podlage

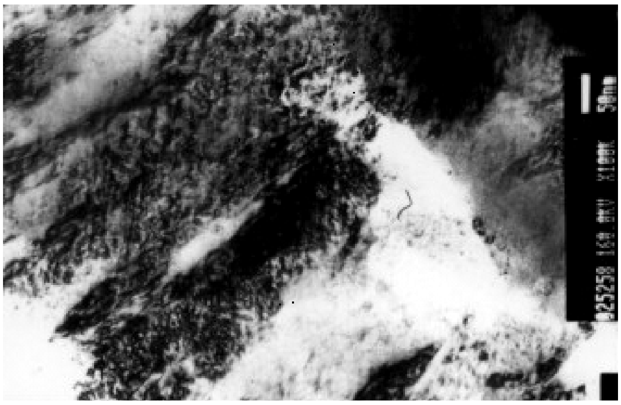


Figure 2: TEM micrograph of the matrix, dislocated martensite, thin foil.
Slika 2: TEM posnetek matrice, dislokacijskega martenzita, tanka folija

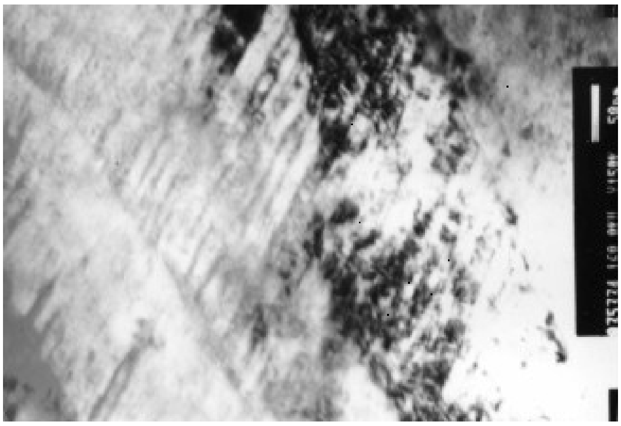


Figure 3: TEM micrograph of the matrix, twinned martensite, thin foil.
Slika 3: TEM-posnetek matrice, martenzitni dvojčki, tanka folija

Besides the fine precipitates, which could not be identified using this experimental technique, the X-ray diffraction revealed two types of carbides, **Figure 4**. To identify the nature of each carbide the thermal history of the material had to be taken into consideration. The as-received Vanadis 6 steel contains the M_7C_3 and MC phases, which behave in different ways during the austenitizing. While the M_7C_3 carbide dissolves almost completely in the austenite during heating to the austenitizing temperature, the MC phase is mainly of primary origin and is dissolved only slowly and to a limited extent. It is therefore assumed that the coarser particles are probably of the MC type, whereas the smaller particles are probably of the M_7C_3 type.

Figure 5 shows how the nitrided layer grows as the processing time and the temperature increase. In the first stage (or if a low temperature and/or a short dwell time is applied) the layer is hardly visible in the micrograph. An increased temperature and/or a longer dwell time can lead to the formation of a nitride network in the near-surface area, as clearly shown in micrographs **5c**

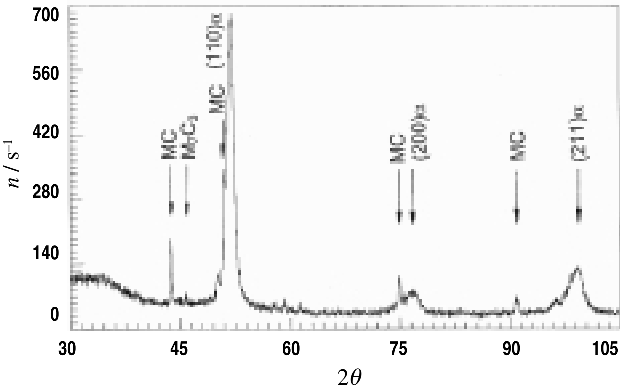
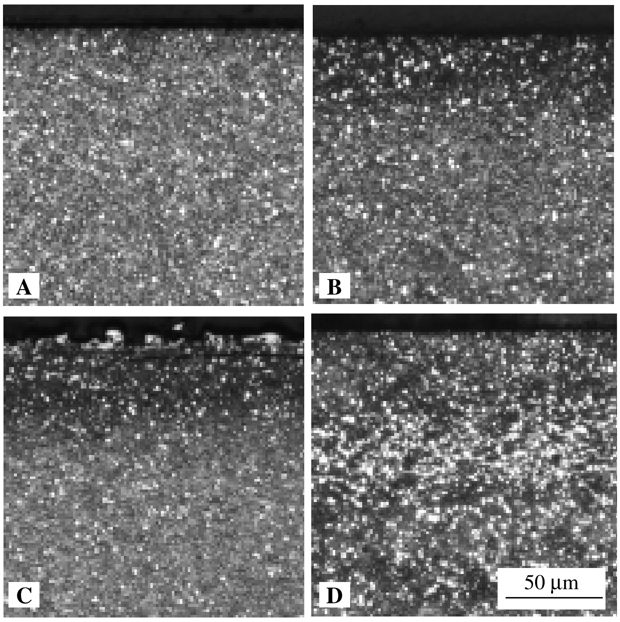


Figure 4: X-ray plot of the substrate
Slika 4: Rentgenski posnetek podlage



A) 470 °C, 30 min; B) 500 °C, 60 min; C) 530 °C, 120 min; D) 570 °C, 120 min

Figure 5: LM micrographs of the nitrided regions, formed under various processing conditions

Slika 5: Optični posnetek nitriranega področja, nastalega pri različnih procesnih parametrih

and 5d. In these micrographs the formation of a compound layer at the surface is also evident. This layer is very thin and appears to be discontinuous. The nitride network close to the surface is also discontinuous and appears only in limited places, where it has a tendency to link the carbide particles.

Generally, the growth kinetics of nitrided regions obeys the rule

$$T = k \cdot t^{-1/2}$$

where T is the thickness and t is the processing dwell time (**Figure 6**).

The development of the phase constitution due to the nitriding begins with the saturation of the α solid solution and the other original phases with nitrogen. After the solid-solubility limit is exceeded, fine nitride particles are formed. As indicated in Table 1, their nature depends on both the temperature and the dwell time, according to the iron-nitrogen phase-diagram. With lower temperatures and shorter nitriding times only the Fe_4N phase is formed. Except for the specimen processed at 530 °C for 30 min, longer times and/or higher temperatures led to the formation of Fe_3N particles in the surface region. There were, however, also indications of chromium-rich nitrides in some cases.

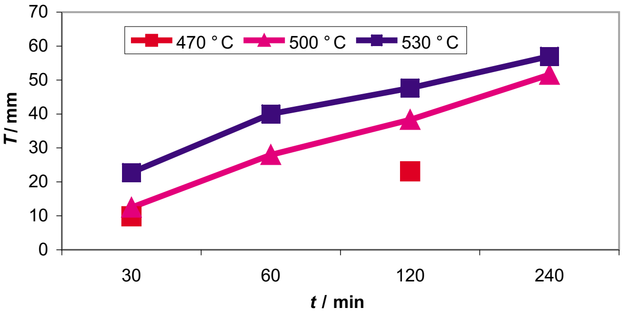


Figure 6: Thickness of the nitrided region as a function of temperature and dwell time

Slika 6: Debelina nitriranega sloja kot funkcija temperature in časa nitriranja

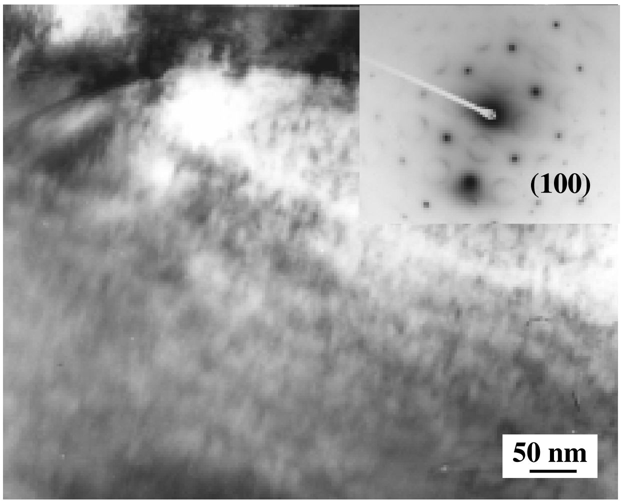


Figure 7: TEM micrograph of a coarse M(C,N) particle

Slika 7: TEM-posnetek velikih M(C,N) delcev

Figure 7 shows a coarse carbo-nitride, which was identified as a vanadium-rich M(C,N) phase with a f.c.c. structure. The rings in the diffraction patterns from the particle are related to the diffuse scattering effect of the short-range-ordered crystal lattice of this phase, in agreement with the observations of Billingam et al. [6.]

Figure 8 shows a second type of coarse particle, which was identified as an orthorhombic variant of the $M_7(C,N)_3$ phase, with the c/a ratio of the orthorhombic

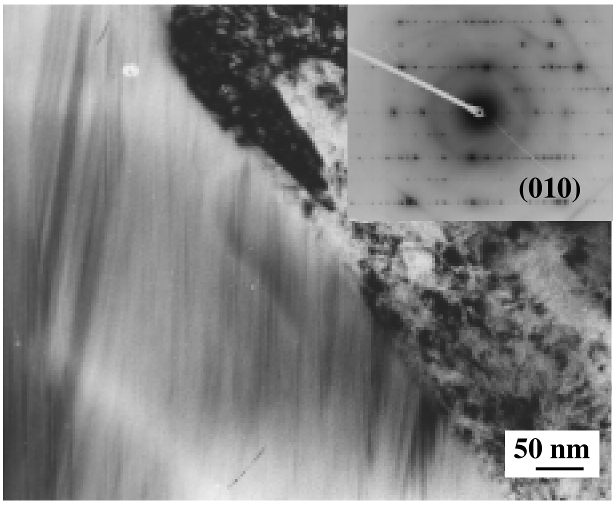
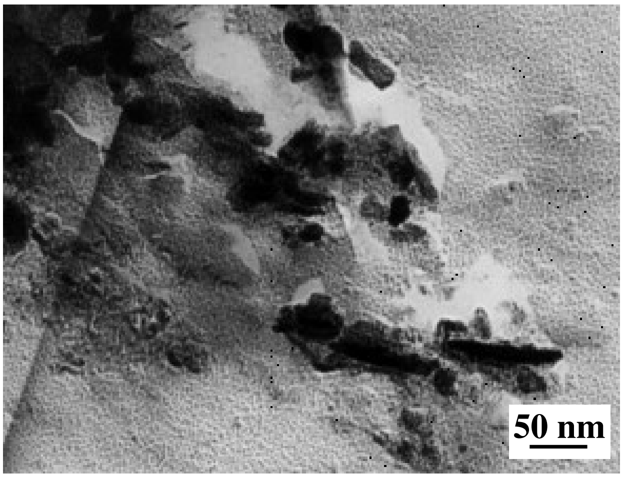


Figure 8: TEM micrograph of a coarse $M_7(C,N)_3$ particle

Slika 8: TEM-posnetek velikih $M_7(C,N)_3$ delcev



Slika 9: TEM-posnetek igličastih nitridov blizu površine, koloidna replika

lattice 1.2 times greater than that of the pure chromium carbide. This lattice expansion has two main reasons: the saturation of the carbide with nitrogen and the substitution of Cr with other alloying elements. As indicated in [1], chromium can be partly replaced by iron and vanadium, which may, together with nitrogen saturation, cause a change in the size of the lattice.

Figures 9 and 10 show TEM micrographs obtained with the collodion-replica technique. Two types of precipitates are evident: needle-like and plate-like particles. Unfortunately, the method only allowed us to extract a limited number of precipitates. This means that reliable information on their density and distribution is not yet available. It was assumed, however, that the precipitates were Fe_4N and Fe_3N.

The saturation of the steel's surface with nitrogen induces two phenomena: the increase in the concentration of nitrogen at the surface and the redistribution of carbon away from the surface. In **Figure 11** the nitrogen- and the carbon-concentration depth profiles for the specimens processed at 470 °C for 30 min and 530 °C for 120 min are shown. A low temperature and/or a short dwell time induced saturation of the surface up to the mass fraction 3 % nitrogen. On the other hand, the processing carried out at 530 °C for 120 min led to a surface saturation exceeding the mass fraction 6 %, with some localised areas being even higher. Such a high nitrogen concentration may correspond to the nitride network (**Figure 5**) that is formed with nitrogen-rich phases. The diffusion zone formed in this way has a thickness of 55 µm. For all of the specimens processed at intermediate temperatures and/or dwell times, the concentration depth profiles showed the mass fraction of N 3–7 % at the surface and a diffusion depth of 20–50 µm.

The carbon-concentration depth profiles have a different shape. Generally, the surface content of carbon is lower than the nominal steel content. It then increases slowly to a maximum value that exceeds that of the nominal one. Beyond the concentration peak, the carbon content decreases slightly to that of the nominal composition of the alloy. For each specimen the position of the maximum peak is situated at the maximum nitrogen diffusion depth. Both the maximum value and

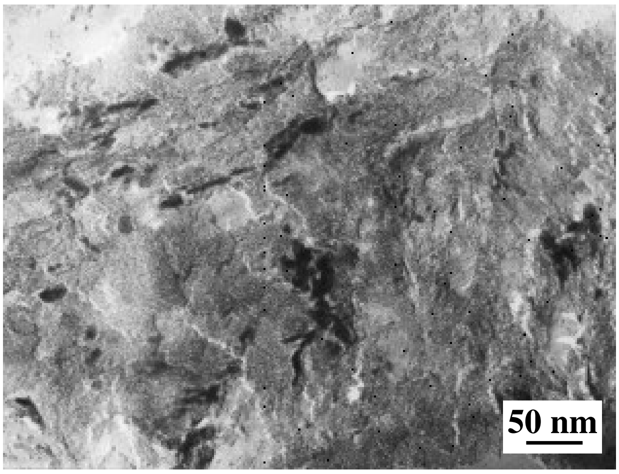


Figure 10: TEM micrograph of the plate-like nitrides in the near-surface region, collodion replica

Slika 10: TEM-posnetek ploščicam podobnih nitridov blizu površine, koloidna replika

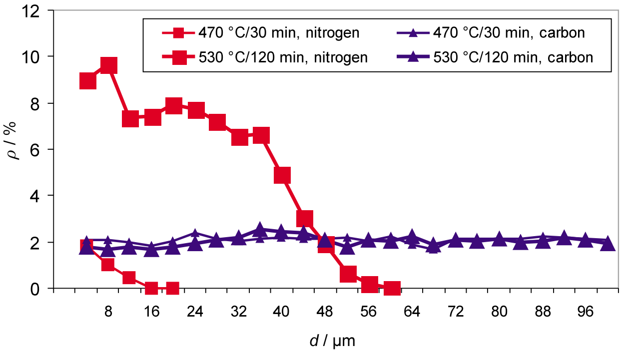


Figure 11: Nitrogen- and carbon-concentration depth profiles for the specimens processed at 470 °C for 30 min and 530 °C for 120 min

Slika 11: Koncentracijski profil dušika in ogljika v globino pri vzorcih, zadržanih pri 470 °C, 30 min in pri 530 °C, 120 min

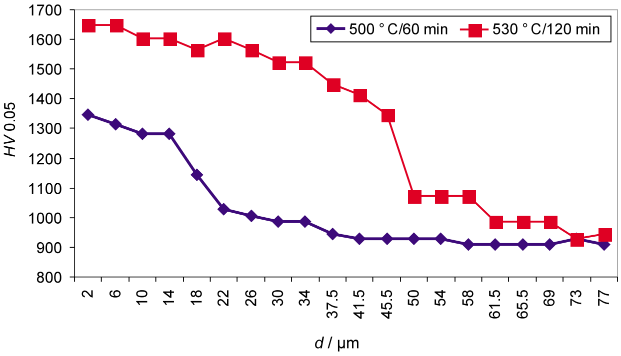


Figure 12: Microhardness depth profiles for various nitriding conditions

Slika 12: Profil mikrotrdote v globino za material, nitriran pri različnih pogojih the slope of the curvature depend on the nitrogen saturation level – the higher the saturation is at the surface the higher is the maximum carbon content.

The saturation of phases with nitrogen and the subsequent formation of nitrides increase the hardness, as shown in **Figure 12**. Measurements revealed a relatively high near-surface hardness even for the specimens treated at lower temperatures and/or short dwell times. For the specimens processed at higher temperatures and/or longer dwell times the near-surface microhardness increases strongly and the maximum values exceeded 1600 *HV* 0.05. The main difference between the specimens processed using various nitriding conditions is that the hardness after processing at lower temperatures drops down at a shorter distance from the surface. On the other hand, only a slight hardness decrease was observed in the specimen processed at 530 °C for 120 min. These differences in microhardness depth profiles are also reflected in the surface hardness, which is markedly lower for the specimens processed at 470 °C (882 *HV* 10) than for those nitrided at 530 °C (1122 *HV* 10).

4 CONCLUSIONS

Before the nitriding, the microstructure consists of a martensite matrix and the carbides M_7C_3 and MC. The martensite is of two types – dislocated and twinned.

The development of phases due to the nitriding generally follows the iron-nitrogen equilibrium diagram. Only if the highest processing temperature is applied do chromium nitride particles form.

The increase in the amount of nitrogen at the surface is considerable and relates to the nitrides that are formed (if any). The input of nitrogen atoms into the surface induces carbon redistribution with carbon moving away from the surface.

Both phenomena induce a considerable surface strengthening – the surface-hardness increase ranges between 180 and 420 *HV* 10, depending on the nitriding conditions used for the material processing.

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