PLASMA NITRIDING OF THE P/M VANADIS 6 STEEL – EFFECT ON MICROSTRUCTURE AND PROPERTIES

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Abstract
The P/M made VANADIS 6 cold work steel was plasma nitrided. Important surface characteristics like the microstructure, the hardness and microhardness, the nitrogen concentration depth profiles, and the phaseoCcurrence and wear behaviour were investigated. The core material consists of MC- and M_7C_3- carbides, uniformly distributed in the matrix. Plasma nitriding led to the increase of both the surface hardness and the microhardness, due to the nitrogen saturation of the thin near surface region. This promotes the formation of Fe_4N- and Fe_3N-nitrides and, at the highest processing temperature and longer time, also the CrN-phase. TheoCcurrence of a nitrogen enriched region at the surface increases the wear resistance. On the other hand, the fracture toughness drops down.
Keywords: P/M tool steels, heat treatment, structural investigation, wear resistance, fracture toughness

INTRODUCTION

The high alloyed P/M made ledeburitic steels have became of great importance because they can extend the lifespan of tools, which leads to significant cost savings [1]. The positive effect of the use of powder metallurgy in tooling is determined by following aspects: After the spraying of molten steel, the liquid droplets solidify under strong non–equilibrium conditions that leads to a restriction of segregation and refinement of the as–solidified microstructure. These phenomena remain after consolidation and subsequent heat treatment of the material as well. The final products then have an excellent combination of microstructural homogeneity and mechanical properties.

The tools made from P/M ledeburitic steels have to be heat treated before use. The hardening and subsequent tempering procedure increases the hardness usually to 700 - 800 HV, which permits the direct use of tools in the production line. The coating, using various PVD methods, may further improve the quality of the manufactured tools [2]. Nevertheless, the use of tools as a part of heavy loaded systems may cause a plastic deformation of the substrate surface where the depth of deformation exceeds the thickness of PVD overlay by many times. Due to the brittleness, the coating can not deform together with the steel surface and may easily fail. Therefore, the efforts leading to an establishment of an optimal processing route of the surface strengthening prior to the PVD were logical. Plasma nitriding is a convenient pre-treatment method before PVD coating, because it allows us to achieve well- defined properties for the nitrided layers [3]. Since the processing temperature is lower than that used for the last tempering cycle, the microstructure and the properties of the core material remain unaffected. A nitrided inter-layer may give rise to mechanical support for the PVD overlay, due to an increased hardness [4, 5]. Published

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papers confirmed an improved adhesion of TiN-PVD coating on the plasma nitrided, both the conventionally produced, and the P/M made M2 grade steel [6,7]. However, there is a lack of information regarding the nitriding behaviour of other P/M ledeburitic steels. Although it was found that the nature of the material plays a dominant role in the diffusion strengthening [8,9], detail of records concerning the mechanical properties and structural characteristics are absent in literature, or published results are often contradictory and do neither correspond to the expected, nor theoretical records and diagrams.

EXPERIMENTAL PROCEDURES

The experimental samples were made from the P/M VANADIS 6 ledeburitic-type steel (2.1% C, 7% Cr, 6% V, Fe bal.). Various types of specimens were prepared, see Tab.1. All the specimens were net-shape machined, and afterwards subjected to a heat treatment bringing the hardness of 60 HRC, unless otherwise designated. The specimens intended for wear testing and also those for the three point bending tests were finished by fine grinding. The metallographical samples were finished by polishing, using an alumina suspension.

Tab.1. List of prepared specimens (*No – non-nitrided).

Set of specimens	Dimensions (mm), purpose	Heat Treatment, plasma nitriding
1	ϕ12x10, structural analysis	1050°C/30 min + 2x 550°C/1 hod, 60 HRC 470, 500, 530°C, 30, 60, 120 and 240 min
2	8x18x70, wear testing	1050°C/30 min + 2x 550°C/1 hod, 60 HRC No
3	8x18x70, wear testing	1050°C/30 min + 2x 550°C/1 hod, 60 HRC 500°C/60 min
4	8x18x70, wear testing	1050°C/30 min + 2x 550°C/1 hod, 60 HRC 530°C/120 min
5	1x10x100, three point test	1000°C/30 min + 2x 550°C/1 hod, 57 HRC, No, 470°C/30 min, 500°C/60 min, 530°C/120 min
6	1x10x100, three point test	1050°C/30 min + 2x 550°C/1 hod, 60 HRC, No, 470°C/30 min, 500°C/60 min, 530°C/120 min
7	3x10x100, three point test	1000°C/30 min + 2x 550°C/1 hod, 57 HRC, No, 470°C/30 min, 500°C/60 min, 530°C/120 min
8	3x10x100, three point test	1050°C/30 min + 2x 550°C/1 hod, 60 HRC, No, 470°C/30 min, 500°C/60 min, 530°C/120 min
9	10x10x100, three point test	1000°C/30 min + 2x 550°C/1 hod, 57 HRC No, 470°C/30 min, 500°C/60 min, 530°C/120 min
10	10x10x100, three point test	1050°C/30 min + 2x 550°C/1 hod, 60 HRC, No, 470°C/30 min, 500°C/60 min, 530°C/120 min

Plasma nitriding was realised on the RUBIG Micropuls – Plasmatechnik® equipment. Standard processes were carried out in cracked ammonia without a nitrogen addition.

The structural analysis were realised using light and scanning electron microscopy. The phase occurrence was investigated by the X-ray diffraction. The surface hardness and microhardness were tested using the Vickers method, with 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 interstitials were established using WDX analysis. The wear tests were carried out using the ring-on-plate method (linear contact between sample and counterbody) under non-lubricated conditions at room temperature. The ČSN 41 4109 (100 Cr 6) ball-bearing steel processed to a hardness of 60 HRC was used as the counterbody material. The testing procedure was performed using a loading of 50 N. The total sliding distance was 10 km, however, the wear rate, represented by the weight loss of the specimens [g], was also examined after 1, 2.5 and 5 km.

The fracture toughness was examined by the three point bending test. That method was chosen because it is very sensitive to any material defects – impurities, segregation, pores etc. The standard testing conditions were: length of the specimens of 100 mm, distance between the supports of 80 mm, loading speed of 1 mm/min, cross section of the specimens – see Tab.1, and testing temperature of 25°C.

RESULTS AND THEIR DISCUSSION

structural investigations

Substrate material consists of the tempered martensite containing fine, uniformly distributed carbides of two types. The first type was determined with the X – ray diffraction as the deficient, vanadium rich MC – phase and the second one as the M_7C_3 – carbide, Fig.1.

The real thickness of the nitrided layer formed at 500°C for 60 min is 25 μm, Fig.2. The layer differs clearly from the substrate, due to the appearance of ultra-fine nitrides in the structure, which leads to intensive etching of the material. Plasma nitriding did not lead to the formation of the compound layer, Fig.3. The micrograph further demonstrates that the diffusion layer can be divided to two areas. Close the surface, there is a region which appears in bright tone. The brightness of microstructure decreases with an increasing distance from the surface. In-between, there is the inter–layer which can be shown in a dark tone, and below that, the substrate material is located.

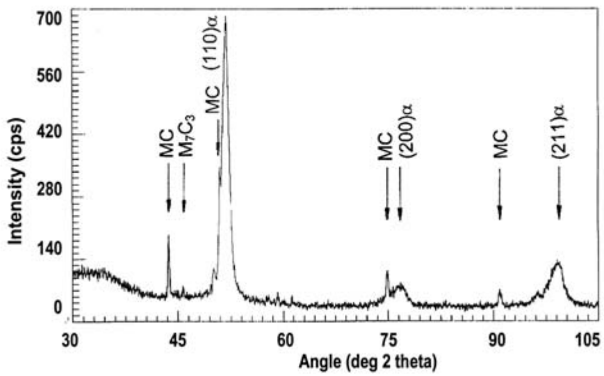


Fig.1. X – ray plot showing the occurrence of the α-Fe solid solution, M_7C_3 and MC in the core material.

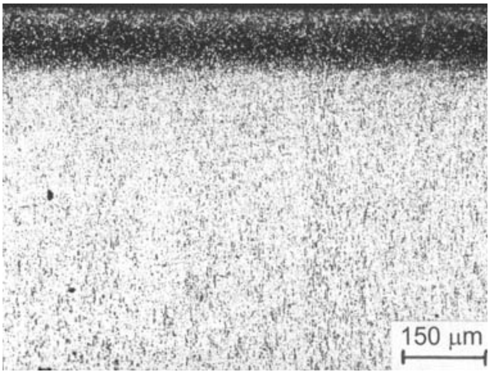


Fig.2. Microstructure of specimen nitrided at 500°C for 60 min

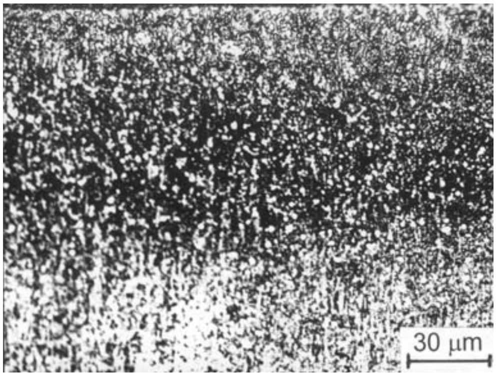


Fig.3. Microstructure of specimens nitrided at 500°C for 60 min (detail from Fig.2).

The phases detected in the non–nitrided steel became saturated by nitrogen. The presence of nitrides depends on both the temperature and the dwell time. If lower temperature and shorter time were to be used, then only the Fe_4N – phase would be formed. Excepting the specimen to be processed at 530°C for 30 min, a longer time and/or higher temperature led to the formation of Fe_3N – nitrides in the surface areas, and also the traces of the chromium rich nitrides were found in some cases.

Figure 4 shows the nitrogen- and the carbon-concentration depth profile for the specimens processed under the following conditions: 470°C/30 min, 500°C/60 min and 530°C/120 min Close to the surface, the nitrogen content exceeds 4 wt.% in all analysed cases. The specimens differ one from each other by the form of curvature. For the specimen processed at 470°C for 30 min, the nitrogen content drops down noticeably, and at a depth of 15 µm, no nitrogen was found. In the case of material processed at 500°C for 60 min, the surface content is 5%, and decreases much more slightly. The presence of N – atoms was not found only at a distance of 45 µm from the surface. The diffusion region formed at 530°C for 120 min contains up to 6 wt. % of nitrogen, and the concentration decreases very slightly with an increasing distance from the surface. The total diffusion depth is about 70 µm. The carbon concentration depth profiles differ from the nitrogen ones considered. Generally, the carbon surface content is much lower than the nominal steel concentration. It increases weakly to the maximal value that clearly exceeds the nominal one. Beyond the concentration peak, the carbon content decreases slightly to that of a nominal alloy composition. For each specimen, the position of the maximum peak is situated to the maximal nitrogen diffusion depth. Both the maximal value and the slope of the curvature depend mainly on the nitrogen saturation of the surface – the higher saturation is at the surface of the higher maximal carbon content.

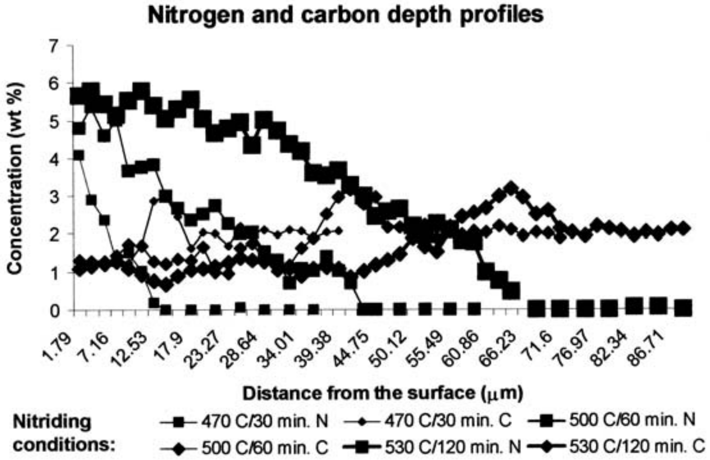


Fig.4. Concentration depth profiles for nitrided specimens.

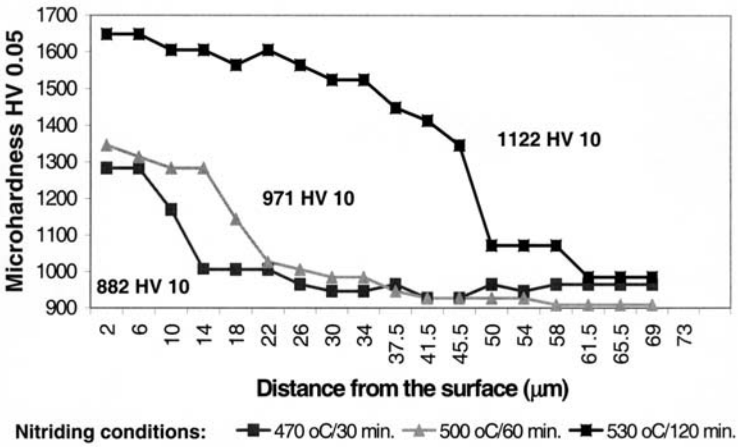


Fig.5. Microhardness depth profiles in nitrided surfaces.

The surface hardness of the non – nitrided material was 700 HV 10. Microhardness measurements revealed relatively high near-surface hardness even for the specimens treated at lower temperature and/or short processing dwell time, Fig.5. For the specimens processed at a higher temperature and/or longer dwell time, the near surface microhardness increases again. Maximal values ranged between 1600 and 1700 HV 0.05. Nevertheless, the microhardness of the material processed at lower temperature drops down significantly, even at a short distance from the surface. On the other hand, only a slight microhardness decrease was observed in the specimen processed at 530°C for 120 min These differences in the microhardness depth profiles are also reflected in the surface hardness, which is markedly lower for specimens processed at 470°C (882 HV 10) than for those nitrided at 530°C (1122 HV 10).

Wear testing

Figure 6 shows that the non – nitrided samples had the highest wear rate. After 10 km sliding, the weight loss exceeded 0.03 g. Nitriding at 500°C for 60 min led to a reduction of the weight loss to 60%. Further improvement can be shown in the case of material treated at 530°C for 120 min Compared to the specimens processed at 500°C, the wear rate is reduced to 50 – 75%.

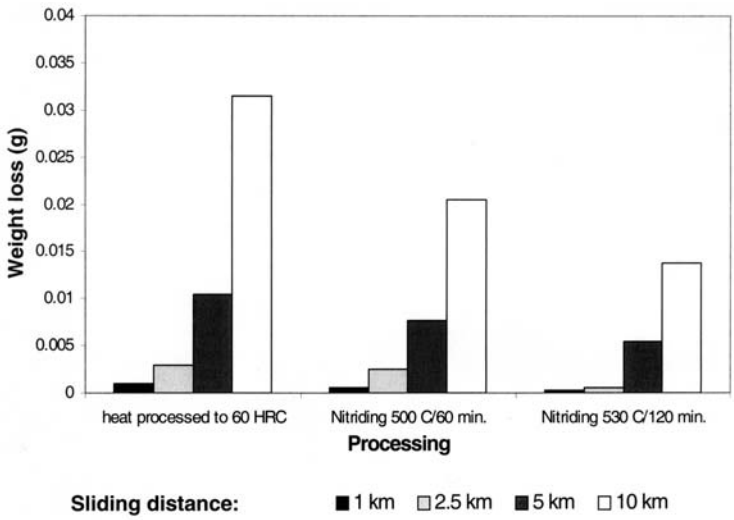


Fig.6. Weight loss of the specimens as a function of sliding distance and surface processing.

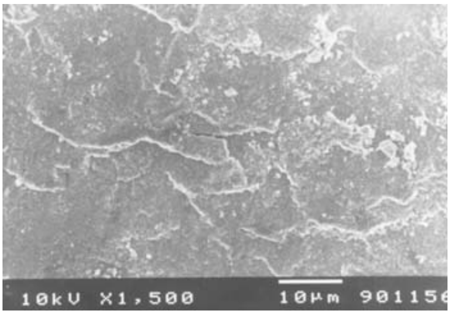


Fig.7. Wear surface of non – nitrided specimen.

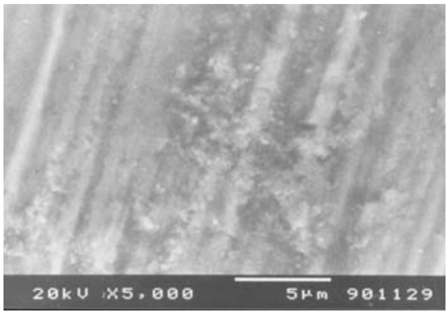


Fig.8. Wear surface of the specimen nitrided at 500°C for 60 min

Figure 7 demonstrates the wear surface of the non – nitrided specimen. The symptoms of stepwise removal of the material are evident. This may be caused by local surface plastic deformation of the material during the sliding. After the plasticity limit of the steel is exhausted, the material is cracked and subsequently removed from the surface. This described process can be held as dominant during the sliding and leads to an intensive wear. Other wear mechanisms like abrasion and fiction did not play any significant role.

Figure 8 shows the surface of the specimen nitrided at 500°C for 60 min Many parallel tracks resulting from the sliding are shown on the micrograph. In addition, on about

30 % of the surface area the symptoms of the “rubbing out” of some fine particles manifests itself. The wear character can thus be described as a combination of the friction and the abrasion, with no symptoms of plastic deformation. With respect to the wear rate measured, it can be said that this wear mechanism causes a lower wear rate in comparison with that of the non – nitrided specimen, Fig.7.

The fact that the wear resistance of nitrided material is better than that of non – nitrided, may be considered as natural. The saturation of original phases by nitrogen, and the formation of nitrides restrict the friction and make the plastic deformation, and subsequent material removal from the surface, more difficult. It also restricts possible plastic deformation and subsequent material removal from the surface. What is interesting is that the specimens processed at 530°C for 120 min had better wear resistance than those nitrided at 500°C for 60 min This is in strong disagreement with the M2 – grade steel [7]. To explain it, the fact that the tempered martensite of the Vanadis 6 steel contains fewer alloying elements than that of M2 material should be taken into account. Lower alloying makes a worsening of the nitriding capability. Higher temperature and/or longer dwell time are required to achieve a strengthening effect equal to the M2 – steel. What is not clear yet, is the fact of whether the wear resistance increases further when a longer time or a temperature above 530°C is applied for the nitriding. Nevertheless, it seems that further prolonging the processing time might not be reasonable, and an application of higher temperature can not be recommended due to the risk of compound layer formation, as well as an exceeding of the tempering temperature.

Fracture toughness and analysis of failure

As shown in Figs.9, 10, the austenitizing temperature plays a dominant role in fracture behaviour of the non-nitrided specimens with a larger cross section. The role of the austenitizing temperature, however, decreases with the decreasing cross section of the specimen. While the difference between the specimens processed at 1000°C, and those processed at 1050°C was 700 MPa in the case of standard specimens, it diminishes to 350 MPa for the flat specimens with a cross section of 3 x 10 mm. If nitrided layer is formed on the surface then the role of austenitizing temperature is minimal, and the presence of the nitrided layer itself and also the layer thickness are the main factors influencing the fracture toughness. It drops down weakly at first but subsequently very rapidly, since the sectional portion of nitrided material increases. For the specimens with a 1 x 10 mm cross section, no influence of the austenitizing temperature was found, Fig.11. The fracture toughness is only influenced by the nitrided layer, whereas the thicker the nitrided layer, the lower the three point bending strength.

The fracture initiation and propagation was realised by the low – energetic ductile mechanism with a dimple morphology of the fracture surface, Figs.12,13. SEM micrograph, Fig.12, shows the local centre of the initiation, located close to the surface in the region where tensile strain acted. Along the surface, there were a lot of such centres found. The fracture propagated in the way of the cavity nucleation at relatively coarse MC- and M_7C_3-carbides, Fig.13.

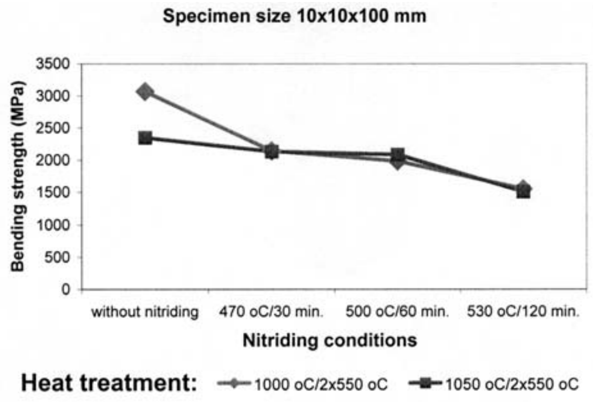


Fig.9. Fracture toughness as a function of the austenitizing temperature and nitriding conditions, specimens 10 x 10 x 100 mm.

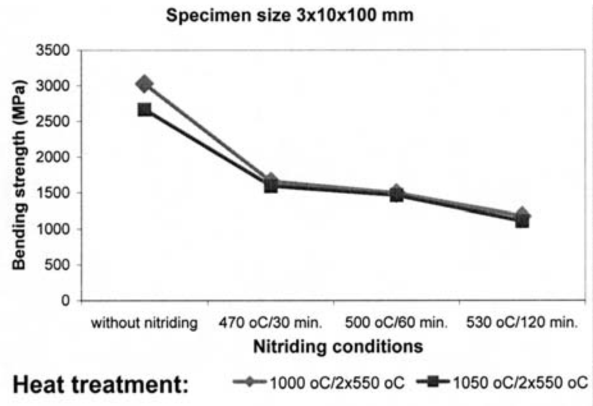


Fig.10. Fracture toughness as a function of the austenitizing temperature and nitriding conditions, specimens 3 x 10 x 100 mm.

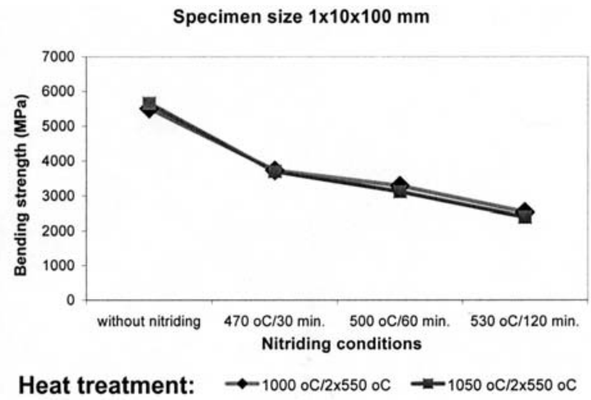
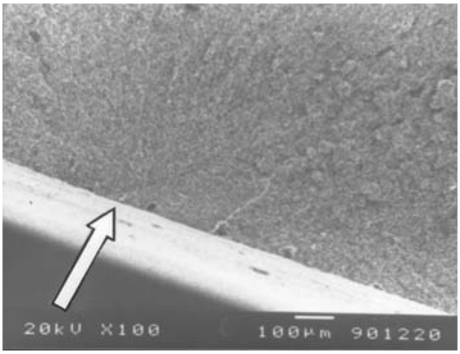
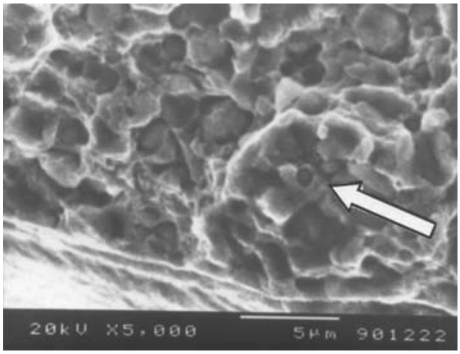
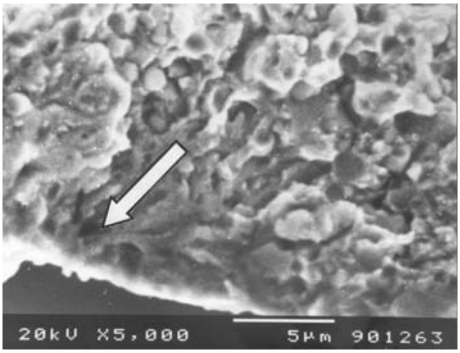


Fig.11. Fracture toughness as a function of the austenitizing temperature and nitriding conditions, specimens 1 x 10 x 100 mm.

The plasma nitriding led to an alteration of the fracture initiation mechanism. The initiation was realised by the transcrystalline cleavage in many centres close the surface. SEM micrograph, Fig.14, illustrates a rugged cleavage facet in such an initiation centre. Transcrystalline cleavage played a dominant role also during the crack propagation, whereas some of the carbide particles were cracked as a result of that process. From the qualitative point of view, changes in the thickness of nitrided layers caused by various processing conditions were reflected primarily in the thickness of the cleavage region. The core material was broken by similar mechanism to that of non – nitrided specimens, see upper part of the micrograph, Fig.14.







⇖ Fig.12. Fracture surface of no-nitrided material.

⇧ Fig.13. Detail from the SEM micrograph from Fig.12.

⇦ Fig.14. Fracture initiation in the nitrided region of material, processed at 470°C for 30 min

The lowering of the fracture toughness due to the formation of a nitrided region can be considered as natural. Nitrided material has an elevated hardness, and it is thus more sensitive to a brittle failure. Nevertheless, the presence of such a region in a near surface area may not always lead to an embrittlement of the specimens. Fox – Rabinovich [5] reported the occurrence of compressive stresses in a nitrided layer formed on the M2 – grade tool steel. These stresses superimpose with those strain – induced, and as a result, may increase the fracture toughness. For the case of Cr – V ledeburitic steels, however, the nitriding capability of the material is not as high as necessary for the compressive stresses formation, and only an embrittlement of the material, due to the appearance of nitrides, takes place during the loading, crack initiation and propagation. What is not clear yet, is whether a longer processing time could induce an improvement of the stress situation in the near surface region, similar to the discussion in the previous chapter.

CONCLUSIONS

Non-nitrided Vanadis 6 steel consists of the tempered martensite and two types of carbides. Provided heat treatment resulted in a hardness of 700 HV 10.

The fracture surface of non-nitrided specimens manifested the symptoms of plastic deformation, although the material had a relatively high hardness.

Plasma nitriding leads to a considerable surface strengthening due to the fine nitrides formed in the near-surface region. The surface hardness increase ranges between 180 and 420 HV 10, depending on the nitriding conditions used for the material processing.

Surface strengthening caused by the plasma nitriding, restricts the plasticity and improves the wear resistance of the material.

The presence of a nitrided layer on the surface lowers the fracture toughness considerably. The thicker the nitrided region, the lower bending strength. This is due to changes of the fracture initiation and propagation in nitrided regions, from the low – energetic ductile mechanism, to that of cleavage.

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