UDK 669.14:621.78
Original scientific article/Izvirni znanstveni članek

ISSN 1580-2949
MTAEC9, 47(1)93(2013)

DIAGNOSTICS OF THE MICROSTRUCTURAL CHANGES IN SUB-ZERO-PROCESSED VANADIS 6 P/M LEDEBURITIC TOOL STEEL

DIAGNOSTIKA SPREMEMB MIKROSTRUKTURE PRI KRIOGENI OBDELAVI P/M LEDEBURITNEGA ORODNEGA JEKLA VANADIS 6

Jana Sobotová[1], Peter Jurči[2], Jan Adámek[3], Petra Salabová[4], Otakar Prikner[4], Borivoj Šuštaršič[5], Darja Jenko[5]

[1]Czech Technical University in Prague, Faculty of Mechanical Engineering, Karlovo nám. 13, 121 35 Prague 2, Czech Republic
[2]Faculty of Material Sciences and Technology in Trnava, Paulínská 16, 917 24 Trnava, Slovakia
[3]Czech Technical University in Prague, Faculty of Nuclear Sciences and Physical Engineering, Břehová 7, 115 19 Prague 1, Czech Republic
[4]Prikner - tepelné zpracování kovů, Martínkovice 279, 550 01, Czech Republic
[5]Institute of Metals and Technology, Lepi pot 11, 1000 Ljubljana, Slovenia
jana.sobotova@fs.cvut.cz

Prejem rokopisa – received: 2012-09-11; sprejem za objavo – accepted for publication: 2012-09-19

Specimens made from P/M Vanadis 6 cold-work steel were austenitized, quenched and tempered for various combinations of the parameters. The selected sets of samples, also in the sub-zero range, were treated at a temperature of –196 °C after quenching. The microstructure was investigated as a function of the austenitizing temperature and the parameters of the sub-zero processing using transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM) and X-ray diffraction. It was found that the as-quenched microstructure is composed of martensite, retained austenite and carbides. The sub-zero processing reduced the amount of retained austenite and led to an increase in the tetragonality of the martensitic lattice. As a result, the hardness of the material was higher by 2 HRc before the tempering of the samples after the sub-zero processing, but the hardness of the sub-zero-processed material after tempering is about 2.5 HRc lower than that of the non-sub-zero-processed steel. Based on the facts that the sub-zero-processed steel contained less retained austenite and an unknown amount of the expected nano-precipitates, we expected it to have a lower capability to manifest the secondary-hardening effect.

Keywords: P/M cold-work steel, heat treatment, sub-zero treatment, precipitates

Vzorci, izdelani iz jekla za delo v hladnem P/M Vanadis 6, so bili avstenitizirani, kaljeni in popuščani pri različnih kombinacijah parametrov. Izbrana skupina vzorcev je bila obdelana v kriogenem področju pri temperaturi –196 °C po kaljenju. Preiskana je bila mikrostruktura v odvisnosti od temperature avstenitizacije in parametrov kriogene obdelave, s presevno elektronsko mikroskopijo (TEM), visoko ločljivo presevno elektronsko mikroskopijo (HRTEM) in z rentgensko difrakcijo. Ugotovljeno je, da kaljeno mikrostrukturo sestavljajo martenzit, zaostali avstenit in karbidi. Kriogena obdelava zmanjša delež zaostalega avstenita in povzroči povečano tetragonalnost martenzitne rešetke. Posledica je povečanje trdote za 2 HRc pred popuščanjem kriogeno obdelanega materiala, po popuščanju tega materiala pa je bila trdota za okrog 2,5 HRc nižja v primerjavi z jeklom brez kriogene obdelave. Na osnovi dejstva, da kriogeno obdelano jeklo vsebuje manj zaostalega avstenita in nepoznano količino nanoizločkov, pričakujemo njegovo manjšo zmožnost za pojav sekundarnega utrjevanja.

Ključne besede: P/M jeklo za delo v hladnem, toplotna obdelava, kriogena obdelava, izločki

1 INTRODUCTION

Vanadis 6 is a powder-metallurgy cold-work ledeburitic tool steel. It is well known that the materials manufactured with powder metallurgy exhibit an extremely refined and homogenous microstructure compared with that of the conventionally produced steels. According to these facts and, also due to its nominal chemical composition, Vanadis 6 has a very high wear resistance, good toughness and high compressive strength. Based on these characteristics, Vanadis 6 is suitable for cutting blades, rolling planes or tools for forming operations.

The structure and properties of ledeburitic steels are determined by the character of the matrix and the type, quantity, size and distribution of carbides and, therefore, the demanded tool life is determined by the conditions of heat treatment. During austenitizing the eutectoid and a part of the secondary carbides are dissolved in austenite, which results in a high hardness of the material after quenching. Other carbides, which are not subjected to dissolution, inhibit the coarsening of the austenite grains and make the steel wear resistant. Bílek et al.[1] reported that there are two types of carbides in Vanadis 6 after austenitizing. The first phase of M_7C_3 carbides underwent the dissolution in the austenite to a greater extent than the second phase of MC carbides, which is stable up to the temperature of 1150 °C. A previous publication[2] states that a higher austenitizing temperature results in an increase in the hardness of Vanadis 6 and a reduction of the three-point bending strength, since the increased austenitizing temperature results in a grain coarsening. After quenching, Cr-V ledeburitic steels contain martensite, retained austenite and undissolved carbides. For a more complete martensitic transformation, sub-zero treatment can be inserted between quenching and tempering.

Recent investigations[3–5] have established that sub-zero treatment does not only substantially reduce the content of retained austenite but also significantly modifies the precipitation behaviour of the carbides in the processed materials. These changes are expected to have a considerable influence on the mechanical properties and, subsequently, on the wear resistance of tool steels. Opinions on the effect of sub-zero processing on the properties of ledeburitic steels differ. Debdulal et al.[3] reported that sub-zero treatment reduces the fracture toughness of the cold-work tool steel AISI D2 that is lower than that of the conventionally heat-treated ones. However, the degree of reduction in fracture toughness varies with the types of sub-zero treatment; it is the lowest for deep, cryogenically treated DCT (–196 °C to –160 °C) specimens and the highest for shallow, cryogenically treated (–160 °C to –80 °C) ones. Fracture-toughness values decrease, expectedly, with an increase in the hardness, a reduction of the retained-austenite content, an increase in the amount of secondary carbides and their size refinement. According to Oppenkowski[4], further investigations on D2 cold-work tool steel show that η-carbides can be observed at higher tempering temperatures, but in some investigations it was impossible to detect any η-carbides. Opposing results have also been obtained with respect to the precipitation of η-carbides. Some investigations found that carbides precipitated after DCT during tempering, others report about the precipitation during the DCT process. Shaohong[5] reported that DCT decreases the retained austenite and increases the hardness and wear resistance of cold-work die steel. Carbon atoms were segregated close to dislocations in the DCT process, ε-carbides precipitated in the twinned martensite during the process of tempering.

The aim of this research is to assess the microstructural changes during the DCT process made to powder-metallurgical tool steel Vanadis 6.

2 EXPERIMENTAL WORK

The nominal chemical composition of the experimental material Vanadis 6, manufactured with P/M is shown in **Table 1**. Details of the experimental heat-treatment program were published elsewhere[6]. Two types of the heat-treatment process were performed. The conventional heat treatment involved the following steps: vacuum austenitizing up to a temperature of 1000 °C or 1075 °C, respectively, and nitrogen gas quenching at a pressure of 5 bar. For the novel heat-treatment process, a sub-zero period at a soaking temperature of –196 °C lasting for 4 h was inserted after quenching and tempering. No tempering was carried out in order to highlight the possible changes in the microstructure of the processed material due to the sub-zero period. A microstructural analysis was performed using a transmission electron microscope TEM JEOL 200CX at an acceleration voltage of 200 kV. Thin foils for the TEM were prepared with an electrolytic jet-polisher (Tenupol) or with an ion slicer. The content of the retained austenite was measured with X-ray diffraction. X-ray patterns were recorded using a Phillips PW 1710 device with Fe-filtered $Co_{\alpha 1,2}$ characteristic radiation. The detector arm was equipped with a monochromator. The data were recorded in the range of 20–144° of the two-theta angle with a 0.05° step and a counting time per step of 5 s.

Table 1: Chemical composition of the investigated steel in mass fractions (*w*/%)

Tabela 1: Kemijska sestava preiskovanega jekla v masni deležih (*w*/%)

Steel	C	Si	Mn	Cr	Mo	V	Fe
Vanadis 6	2.1	1.0	0.4	6.8	1.5	5.4	balance

3 RESULTS AND DISCUSSION

The mechanical properties obtained after different steps of the heat treatment are summarized in **Table 2** [2,6]. Although the hardness is approximately the same after quenching and after quenching and sub-zero processing at both austenitizing temperatures, the hardness of the sub-zero-processed material after tempering is by about 2.5 HRc lower than that of the non-sub-zero-processed steel.

The tempering of the material induced different behaviours of the non-sub-zero- and sub-zero-processed steels. Generally, the non-sub-zero-processed steel had a higher hardness than the sub-zero-processed one. We assume that, firstly, the occurrence of a high number of nano-particles and, secondly, a lower share of the retained austenite are responsible for the deterioration of the secondary hardenability of the material. This seems to be logical because the secondary hardenability can be considered as a comprehensive effect of the tempering of martensite (hardness decrease), transformation of the retained austenite to martensite (hardness increase) and precipitation of carbides (hardness increase). Based on the facts that the sub-zero-processed steel contained a lower share of the retained austenite and an expected large number of nano-precipitates, we anticipated its capability to manifest the secondary-hardening effect to be lower.

Figure 1 shows a bright-field image of the microstructure of the specimen quenched from 1000 °C without DCT and tempering. The matrix of the material apparently has a two-phase structure. The main structural constituent is the twinned martensite, which is typical for high-carbon steels. The second structural feature of the matrix is the retained austenite as shown in the dark-field image of the area, **Figure 2**. The fact that the material after quenching, without DCT, contains a large amount

Table 2: Hardness and bending strength of differently heat-treated specimens[2,6]
Tabela 2: Trdota in upogibna trdnost različno toplotno obdelanih vzorcev[2,6]

Austenitizing temperature	Hardness A HRc	Sub-zero processing	Hardness B HRc	Hardness C HRc	Bending strenght MPa
1000 °C	66.0	no		59.0	3564
1075 °C	66.0	no		63.0	2768
1000 °C	65.0	–196 °C/4 h	66.0	56.5	3272
1075 °C	65.5	–196 °C/4 h	67.0	60.5	3087
Hardness A	hardness after quenching				
Hardness B	hardness after quenching and sub-zero processing				
Hardness C	hardness after complete heat treatment with a double tempering at 530 °C/2 h				

of retained austenite could have been expected. During austenitizing some of the carbides are dissolved and the austenite becomes saturated with carbon and alloying elements. This induces a lowering of both the M_s and M_f temperatures of Cr-V ledeburitic steels, whereas M_f lies well below the freezing point. As a result, the martensitic transformation is not fully completed. The diffraction patterns from both structural constituents are shown in **Figures 3** and **4**.

After quenching from the austenitizing temperature of 1000 °C and DCT at –196°C/4 h, the matrix again has a two-phase structure as seen in **Figures 5** and **6**. This means that even the sub-zero processing does not completely remove the retained austenite from the structure. This could be evidently expected. From the physical-

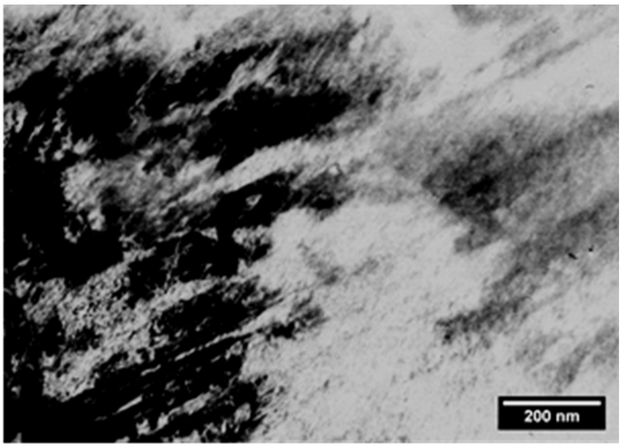

Figure 1: Microstructure of Vanadis 6 after quenching from 1000 °C without DCT and tempering – TEM bright-field image
Slika 1: Mikrostruktura Vanadis 6 po kaljenju iz 1000 °C, brez DTC in popuščanja (TEM – svetlo polje)

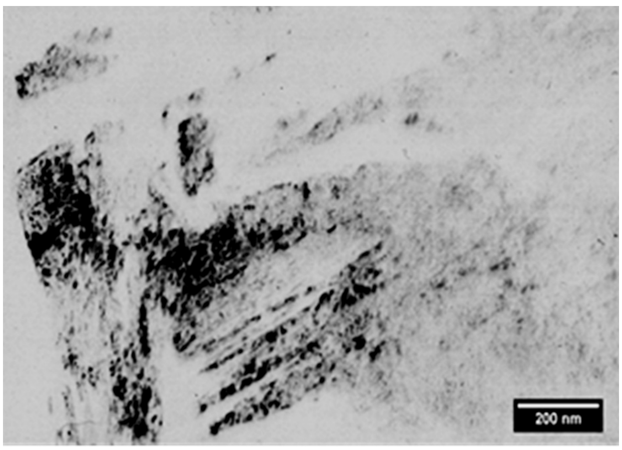

Figure 2: Microstructure of Vanadis 6 after quenching from 1000 °C without DCT and tempering – TEM dark-field image
Slika 2: Mikrostruktura Vanadis 6 po kaljenju iz 1000 °C, brez DCT in popuščanja (TEM – temno polje)

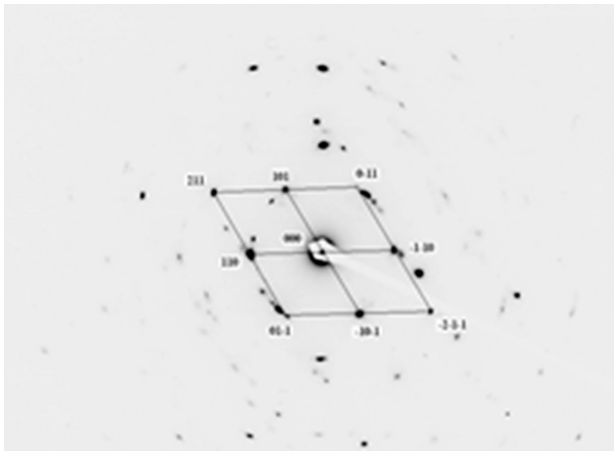

Figure 3: Electron-diffraction patterns from martensite
Slika 3: Uklonska slika martenzita

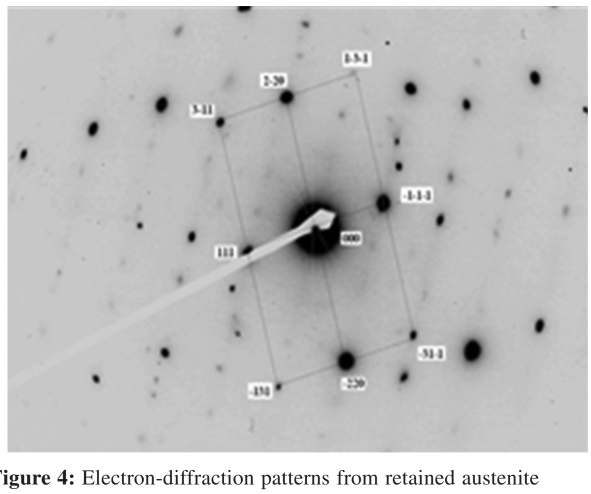

Figure 4: Electron-diffraction patterns from retained austenite
Slika 4: Uklonska slika zaostalega avstenita

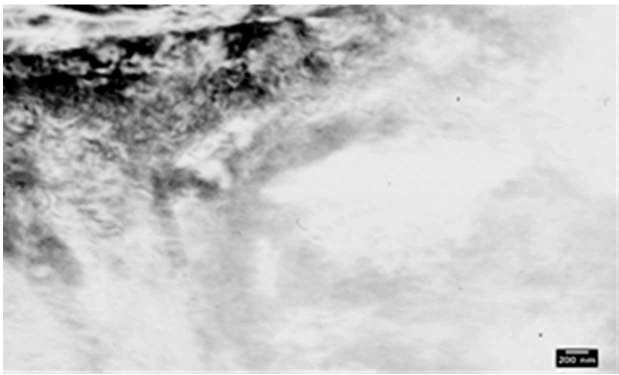

Figure 5: Microstructure of Vanadis 6 after quenching from 1000 °C and DCT without tempering – TEM bright-field image
Slika 5: Mikrostruktura Vanadis 6 po kaljenju iz 1000 °C in DCT, brez popuščanja (TEM – svetlo polje)

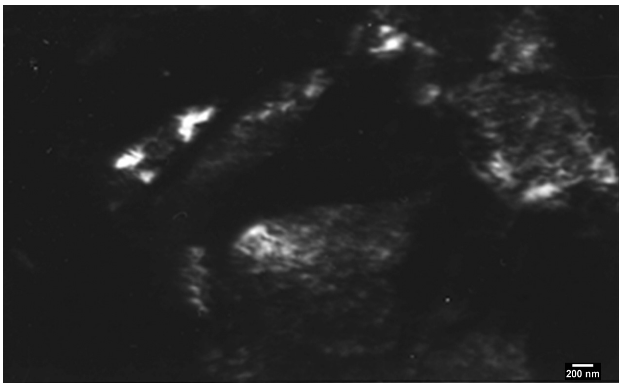

Figure 6: Microstructure of Vanadis 6 after quenching from 1000 °C and DCT without tempering – TEM dark-field image
Slika 6: Mikrostruktura Vanadis 6 po kaljenju iz 1000 °C in DCT, brez popuščanja (TEM – temno polje)

metallurgy viewpoint the martensitic transformation cannot be fully completed and after quenching a certain share of the retained austenite will always remain in the structure. The problem is how to minimize the content of the retained austenite. Transmission microscopy, however, will never precisely quantify the content of the retained austenite.

A quantification of the amount of the retained austenite was performed with an X-ray diffraction analysis, the results are in **Table 3**.

Besides the martensite and the retained austenite, MC (or M_4C_3) and also M_7C_3 carbides were found in the structure. The contents of these carbides were found to be independent of the use (or no use) of DCT in the heat-treatment cycle. This is logical since it is the austenitizing temperature that plays a substantial role in the changes in the volume fraction of these carbides. On the contrary, a large difference was found in the contents of the retained austenite and martensite. The content of the retained austenite was almost three times lower for the DCT material than for the non-DCT material. It is thus evident that DCT really contributes to a marked decrease in the amount of the retained austenite in the structure of the material after the heat treatment with DCT. At the same time, a higher supersaturation of the martensite occurred due to DCT – the degree of tetragonality c/a was found to be much higher for the DCT material.

Besides deformation twins, a dense dislocation network can also be found in the martensite needles. This was well apparent at high magnification in **Figures 7** and **8**. The dislocation network prevents the identification of the potential minority phases, so that, at this stage of the research, the assumed precipitation of carbide nanoparticles during the DCT, often published in literature, could not be confirmed. On the other hand, the presence of such a high number of dislocations is a sign of a high plastic deformation and an apparently high stress in the crystal lattice. Plastic deformation can induce various processes, e.g., self-tempering of martensite accompanied by a formation of carbide nanoparticles.

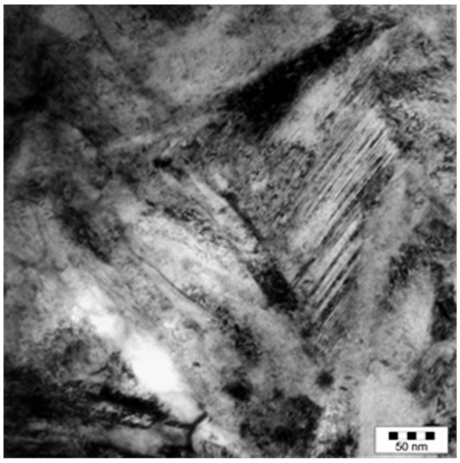

Figure 7: Microstructure of Vanadis 6 after quenching from 1000 °C and DCT without tempering – TEM bright-field image – a detail
Slika 7: Detajl mikrostrukture Vanadis 6 po kaljenju iz 1000 °C in DCT, brez popuščanja (TEM – svetlo polje)

Table 3: Results of an X-ray diffraction of Vanadis 6 after quenching from the temperature of 1075 °C and sub-zero processing at –196 °C/4 h
Tabela 3: Rezultati rentgenske difrakcije Vanadis 6 po kaljenju iz temperature 1075 °C in kriogeni obdelavi pri –196 °C/4 h

Heat treatment	Content of martensite, *w*/%	Content of retained austenite, *w*/%	Lattice parameter of martensite (nm) degree of tetragonality *c/a*	Other phases
Quenching	49.45	17.76	a = 0.28623, c = 0.29154 c/a = 0.101186	MC (M_4C_3) M_7C_3
Quenching + DCT	63.1	6.1	a = 0.28596, c = 0.29234 c/a = 0.10223	MC (M_4C_3) M_7C_3

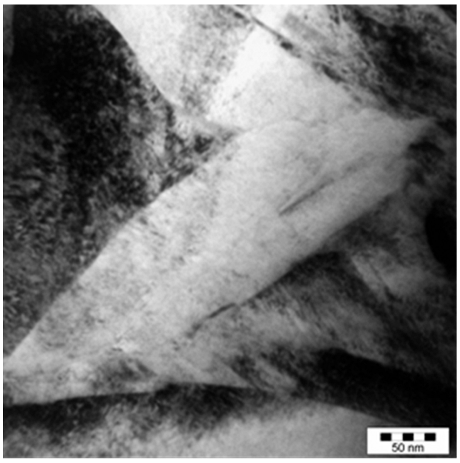

Figure 8: Microstructure of Vanadis 6 after quenching from 1000 °C and DCT without tempering – TEM dark-field image – a detail
Slika 8: Detajl mikrostrukture Vanadis 6 po kaljenju iz 1000 °C in DCT, brez popuščanja (TEM – temno polje)

This could explain the assumed higher stresses in the lattice and the similarly high dislocation density in the martensite obtained with DCT, **Figures 7** and **8**.

It was shown that the magnification of a standard TEM is not sufficient for the identification of the assumed precipitation of carbide nanoparticles. According to this, we tried to investigate the assumed precipitation of carbides, often recorded in literature, with HRTEM, **Figures 9** and **10**.

On the left-hand side of **Figure 9** there is a typical contrast between an amorphous layer and some faint underlying fringes of the crystal planes. To the right the contrast passes to Moire fringes due to the superimposed, twisted crystal lattices. A Moire pattern is also in the bottom right-hand corner of the micrograph. In the central part of the lattice the fringes are not clear, perhaps due to some internal strains. Their clearest contrast is in the top right-hand corner. However, the atomic columns are not parallel to the electron beam and so no dots, but only fringes, are visible.

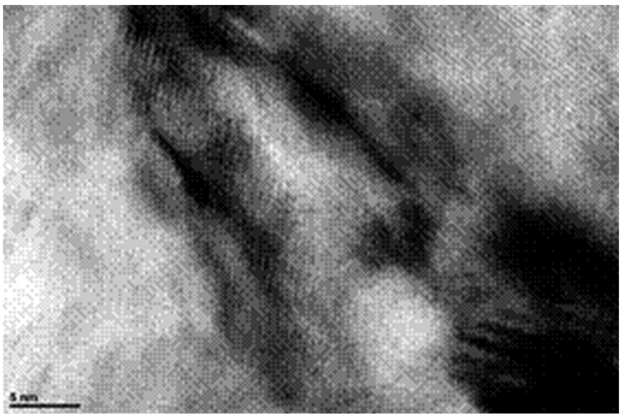

Figure 9: Microstructure of Vanadis 6 after quenching from 1000 °C and DCT without tempering – HRTEM
Slika 9: Mikrostruktura Vanadis 6 po kaljenju iz 1000 °C in DCT, brez popuščanja (HRTEM)

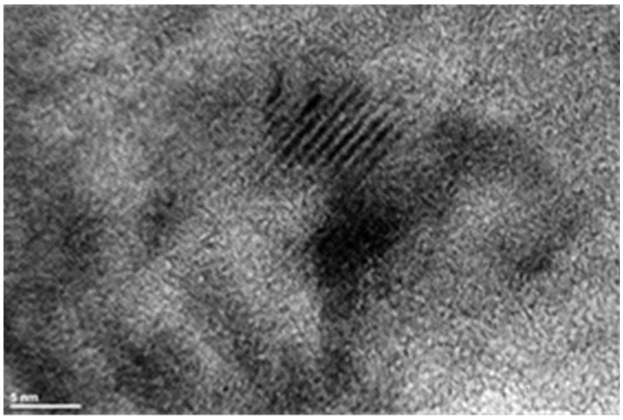

Figure 10: Microstructure of Vanadis 6 after quenching from 1075 °C and DCT without tempering – HRTEM
Slika 10: Mikrostruktura Vanadis 6 po kaljenju iz 1075 °C in DCT, brez popuščanja (HRTEM)

In the central part of **Figure 10** there is a dot contrast between the atomic columns, probably in the 111-Fe projection. The regular pattern in the upper central part could be a nanotwinned region or a Moire pattern caused due to the superimposed, twisted crystal lattices or a faulted nanoparticle. However, the contrast is not clear enough to allow an unambiguous interpretation.

The expected nano-precipitates could not even be confirmed by using HRTEM. Neither did the results of EDS analyses show the differences between the materials after quenching and after quenching and DCT.

In the next investigation we will turn our attention to the assessment of microstructural changes after tempering the sub-zero-processed cold-work tool steel Vanadis 6. Such a research might answer the question as to whether it is possible to identify the nanoparticles in the structure after a complete heat treatment including DCT, often addressed in literature.

4 CONCLUSIONS

- The content of the retained austenite was almost three times lower for the DCT Vanadis 6 than that without DCT.
- At the same time, a higher supersaturation of martensite occurred due to DCT – the degree of tetragonality c/a was found to be much higher for the DCT material.
- Using TEM it was proved that the dislocation network prevents the identification of potential minority phases in the microstructure of the DCT material.
- The expected nano-precipitates in the microstructure of the DCT material could not be confirmed, even by using HRTEM.
- For the next investigation we recommend an assessment of the microstructural changes after tempering the DCT cold-work tool steel Vanadis 6.

Acknowledgements

The authors wish to thank the Ministry of Industry and Trade of the Czech Republic for the financial support given to the Project TIP FR-TI1/003. The paper was created within the research MSM6840770021 "Diagnostic of materials" and project OPPA CZ.2.17/1.1.00/32213 "Qualifications of the academic workers from CTU in Prague in science and research".

5 REFERENCES

[1] P. Bílek, J. Sobotová, P. Jurči, Evaulation of Structural changes in Cr-V Ledeburitic Tool Steels Depending on Temperature Austenitization, Mater. Tehnol., 44 (**2011**) 4, 33–37

[2] P. Jurči et al., Effect of Sub-zero Treatment on Mechanical Properties of Vanadis 6 PM Ledeburitic Tool Steel, in Metal 2010: 19th International Conference on Metalurgy and Materiále, Roznov pod Radhostem

[3] D. Debdulal et al., Influence of sub-zero treatments on fracture toughness of AISI D2 steel, Materials Science and Engineering A, 528 (**2010**), 589–603

[4] A. Oppenkowski, S. Weber, W. Theisen, Evaluation of factors influencing deep cryogenic treatment that affect the properties of tool steels, Journal of Materials Processing Technology, 210 (**2010**), 1949–1955

[5] L. Shaohong et al., Influence of deep cryogenic treatment on microstructure on microstructure and evaluation by internal friction of tool steel, Cryogenics, 50 (**2010**), 754–758

[6] J. Sobotova et al., Structure and properties of sub-zero processed Vanadis P/M ledeburitic tool steel, in Metal 2011: 20th Anniversary International Conference on Metalurgy and Materilas, Brno