



SUB-ZERO TREATMENT OF P/M VANADIS 6 LEDEBURITIC TOOL STEEL

Peter Jurči^{1,*}, Jana Sobotová², Petra Salabová³, Otakar Prikner³, Borivoj Šuštaršič⁴, Darja Jenko⁴

¹ Faculty of Material Sciences and Technology in Trnava, Paulínská 16, 917 24 Trnava, Slovakia

² Czech Technical University in Prague, Faculty of Mechanical Engineering, Karlovo nám. 13, 121 35 Prague 2, Czech Republic

³ Prikner - tepelné zpracování kovů, Martinkovice 279, 550 01, Czech Republic

⁴ Institute of Metals and Technology, Lepi pot 11, 1000 Ljubljana, Slovenia

* corresponding author: e-mail: p.jurci@seznam.cz

Resume

The Cr-V ledeburitic steel Vanadis 6 was vacuum austenitized at different temperatures, nitrogen gas quenched and double tempered at 530 °C for 2 h. For the selected samples, a sub-zero period was inserted between quenching and tempering. The obtained results infer that: I) as-quenched microstructure consisted of martensite, retained austenite and undissolved carbides, II) sub-zero processing reduced the amount of the retained austenite and increased the tetragonality of the martensitic lattice, III) as-quenched hardness of the steel was higher by 2 – 3 HRC due to sub-zero processing, IV) as-tempered hardness increased with increasing austenitizing temperature but it decreased slightly with the sub-zero period, V) no negative impact of sub-zero processing on toughness was recorded, VI) wear resistance increased with sub-zero period when 100Cr6 steel has been used as a counterpart.

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1. Introduction

Conventional heat treatment (CHT) of Cr-V ledeburitic steels involves austenitizing, hold at desired temperature, quenching and several times tempering. During the austenitizing, eutectoidal and a part of secondary carbides undergo dissolution in the austenite. This increases the saturation of the solid solution with carbon and alloying elements and results in higher as-quenched hardness. Other part of carbides, which does not undergo the dissolution, hinders the austenite grains coarsening and makes the steels wear resistant. After quenching, the materials contain martensite (α'), retained austenite (γ_R) and undissolved carbides [1]. A part or whole amount of γ_R (depending on tempering temperature) converts into the α' during subsequent tempering. Moreover, precipitation

of carbides from supersaturated solid solutions takes place during tempering. Both phenomena result in so-called secondary hardening effect. Saturation of the austenite lowers the characteristic martensite start (M_s) and martensite finish (M_f) temperatures so that latter lies often well below the ambient temperature. CHT is insufficient to convert higher amount of austenite into martensite, which leads to unacceptable portion of γ_R in the steel after quenching. For a more complete martensitic ($\gamma - \alpha'$) transformation, sub-zero treatment (SZT) can be inserted between quenching and tempering.

Almost 40 years ago, Berns [2] reported a significant hardness increase for sub-zero processed X210CrW12, X290Cr12 and X165CrV12 steels, respectively. Moreover, a shift of the secondary hardness peaks to lower

tempering temperatures has been established. Recent investigations established some metallurgical aspects of the SZT and its impact on the structure and properties of Cr- and Cr-V steels, respectively. However, there are adverse results on the improvement of several mechanical properties and, the mechanisms postulated as being responsible for the improvement, also. The reasons of that are mainly:

- The use of different materials for the investigations, hence, there is no comprehensive study on the effect of SZT on the structure and properties of ledeburitic steels, with a minor exception being represented by classically manufactured D2-grade steel.
- Different heat treatment regimes used in the investigations. For instance, for the D2-grade steel, Das et al. [3 - 9] have used a temperature of 1025 °C for the austenitizing while Pellizzari and Molinari [10] have carried out the austenitizing at 980 °C. In the SZT, some investigations were done using temperatures of -75 °C and -125 °C, respectively [4, 9] while others have been conducted at -196 °C [3, 5 - 8, 10]. The soaking times were very different, also. They ranged from short times, namely 5 min or 1 h up to very long periods (tens hours). There is a strong disagreement with respect to recommended cooling/heating regime from an ambient temperature to the lowest one and back – some authors have kept both the cooling and the heating rate at 0.75 °C/min [3 - 9] but no consensus with respect of this parameter is available in other works [10 - 12]. Finally, the tempering has been carried out at different temperature / time regimes, also.

The D2 grade Cr-ledeburitic tool steel is the most commonly used material for the investigations. For this material, it has been

established that the SZT results in moderate increase in as-tempered hardness (note, that the tempering has been performed at 210 °C for 2 h) [3] and improves the dimensional stability of components [11]. The fracture toughness K_{IC} was reduced significantly due to the SZT when it was performed at -75 °C and -125 °C, respectively, while the reduction of the fracture toughness was marginal after SZT at -196 °C [4]. Das et al. [5 - 8], Oppenkowski [12] and Stratton [13] reported considerably improved wear performance of SZT D2-steel, with the maximum improvement at 36 h treatment.

The current state of knowledge is that the improvement in properties can be attributed to the following alterations in the substructure: i) more complete $\gamma - \alpha'$ transformation, ii) alterations in the lattice parameters of the α' resulting from extensive plastic deformation of the martensite during the low-temperature martensitic transformation and possible carbon clustering at moving dislocations [14], iii) precipitation of nanosized coherent η -carbides (note, that there are ambiguities over latter phenomenon – some authors suggested the carbides precipitation during the sub-zero period [15] but others during subsequent tempering [4, 14, 16]). In addition, there are inconsistent opinions on the nature of these particles – besides the precipitation of η -carbides the presence of ε -carbide after low temperature tempering has been suggested as possible [14, 16]), iv) higher population density (and refinement) of small carbides in as-tempered SZT material [9, 17].

The SZT of other Cr- and Cr-V-ledeburitic steels has been investigated less systematically. Moreover, the results are incomparable with those obtained on the D2-steel since different heat treatment regimes have been used for the material processing. The main findings are summarized in Table 1.

Table 1

Main findings concerning the SZT of Cr- and Cr-V ledeburitic steels others than the D2-grade material.

Material	Source	Processing	Main results of SZT
Vanadis 6	[18 - 20]	Austenitizing 1000-1075 °C, SZT -196 °C / 4, 10 h, tempering 2 x 530 °C / 2 h	Moderate increase in K_{IC} marginal as-quenched hardness increase, as-tempered hardness decrease, marginal improvement in three point bending strength
D3	[21]	Austenitizing not available, SZT -180 °C, -140 °C, -110 °C / 6, 24 h, tempering 1x150 °C / 2 h	Several times improved wear resistance compared to CHT, no structural investigations
X110CrMoV82	[10]	Austenitizing 980 °C/35 min, SZT -196 °C/35 h, tempering 2x, 1 st 500 °C / 3 h, 2 nd 510 °C / 2 h.	Improvement of wear resistance in tens of percents Highlighted secondary hardness peak
X220CrVMo 13-4	[16]	Austenitizing 1080 °C/ 20 min, SZT -196 °C / 24, 36, 48 h, no tempering	Refinement of α' due to SZT Carbon atoms immobile below -50 °C Dislocation mobility decreases with increased low-temperature holding time High dislocation density of martensite (SZT), extensive plastic deformation of virgin martensite in SZT

2. Experiment

The experimental material was the PM ledeburitic steel Vanadis 6 (2.1 % C, 1.0 % Si, 0.4 % Mn, 6.8 % Cr, 1.5 % Mo, 5.4 % V and Fe as balance). The samples for microstructural investigation were cylinders with 17 mm in diameter and a height of 10 mm. The second type of samples was the three point bending specimens of a size 10x10x100 mm, fine ground to $R_a = 0.2 - 0.3 \mu\text{m}$. The CHT involved the vacuum austenitizing up to temperatures from the range 1000 - 1075 °C, hold at a given temperature for 30 min., nitrogen gas quenching at 5 bar pressure and 2x tempering at 530 °C / 2 h. SZTs have been inserted between quenching and tempering and their parameters were as follows: -90 °C / 4 h, -196 °C / 4 h and -196 °C / 10 h. The microstructure and fracture surfaces were recorded using the scanning electron microscopy (SEM). The content of the γ_R was measured by X-ray diffraction. X-ray patterns were recorded using Fe filtered $\text{Co}_{\alpha 1,2}$ characteristic radiation, in the range 20 – 144° of the two-theta angle. It should be

emphasized that for X-ray analysis, the samples without tempering were used. Hardness has been measured by Rockwell C method. Three point bending tests have been carried out at following parameters: the distance between supports was 80 mm, loading in the central region and loading rate of 1 mm / min, up to the moment of the fracture. Five specimens were used for the testing at any combination of heat treatment parameters. The mean value and statistical uncertainty of the bending strength (σ_B) were calculated. Wear tests have been performed with a CSM pin-on-disc tribometer, at a normal loading of 5 N, ambient temperature and dry conditions, respectively. The wear track radius was 2 mm. The balls with a diameter of 6 mm, made of 100Cr6-steel (hardness of 735 HV 10) were used as the counterparts. Experiments were done on 3 samples for each combination of heat treatment parameters.

The wear rate was determined according to standardized method described in ASTM G 99 – 95a Standard [22].

3. Results and Discussion

The microstructure of the Vanadis 6 steel is composed of the matrix and two types (M_7C_3 , MC) of carbides, Fig. 1. The MC-phase (medium sized particles) forms eutectic part of the carbides mostly. The M_7C_3 -phase underwent the dissolution in the austenite, being responsible for the saturation of the austenite with carbon and alloying elements. The portion of dissolved carbides increases as the austenitizing temperature increases, Fig. 1a, b. Other part of the M_7C_3 -carbides (designated as large secondary carbides (LSCs) and small secondary carbides (SSCs), and almost complete amount of MC-phase remained undissolved. The matrix is composed of the martensite and γ_R , Fig. 1a, b, Table 2. The volume fraction of γ_R increases with increasing austenitizing temperature (T_A) expectedly since higher T_A tends towards higher saturation of austenite and lowering of the M_f temperature well below zero. The as-tempered microstructure of matrix differs from that as-quenched – it is composed of tempered martensite with well visible needle-like formations, Fig. 1c.

Table 2 shows important structural characteristics of the material summarized for as-quenched ($T_A = 1000$ °C) and as-quenched and SZT steel. It is evident that the amount of γ_R decreased almost three times and the tetragonality of σ' increased, respectively, with the application of the SZ processing.

Increased tetragonality of the martensite after SZT is rather inconsistent with the observations published by Tyshchenko et al. [16] and Gavriljuk et al. [14]. However, direct comparison of obtained results is only roughly possible because:

- in both papers [14, 16], different tool steels, namely X220CrVMo 13-4 and D2-grade, have been used,
- in the paper [14], low-temperature X-ray diffraction has been used for the

determination of the tetragonality of martensite while the data given in Table 1 have been recorded after re-heating of the material up to a room temperature,

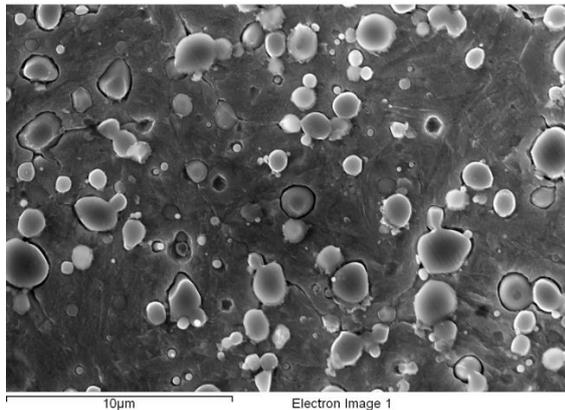
- it is worth noticing that the data on lowered tetragonality of the martensitic lattice have not been obtained on ledeburitic tool steels but on the X100Mn6 steel, which makes the results incomparable, also.

However, a possible interpretation of adverse results on the tetragonality of the α' is available and is based upon the following considerations: Low-temperature martensitic transformation is accompanied with extensive plastic deformation of freshly formed martensite, resulting in enhanced dislocation density inside the martensitic domains produced by the SZT, compared to those formed via the CHT. This fact was confirmed for the Vanadis 6 steel by our current investigations but the results were not published yet. Plastic deformation of virgin martensite is most decidedly accompanied with a capture of carbon atoms (immobile at very low temperatures) by moving dislocations and, as a result, with a formation of carbon clusters at the lattice defects. It is thus logical that these carbon clusters make a depletion of the martensite by carbon and reduce its tetragonality as a consequence. Subsequent increase of the tetragonality of the α' can be then due to an ageing of the martensite on the re-heating from the temperature of the SZT up to the room temperature. This ageing is very probably connected with lattice distortion at the interfaces of high-carbon containing martensite (resulting from carbon clusters) and surrounding low-carbon martensite. Some of our experimental results obtained on the Vanadis 6 steel have brought indications of the presence of both the high-carbon and the low-carbon martensite, also [24].

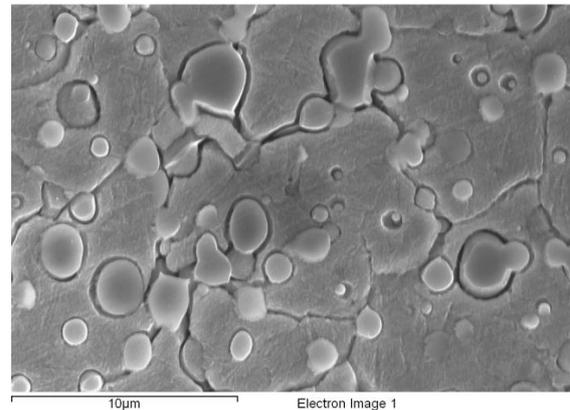
Table 2

Microstructural parameters of no sub-zero and sub-zero processed material ($T_A = 1000^\circ\text{C}$).

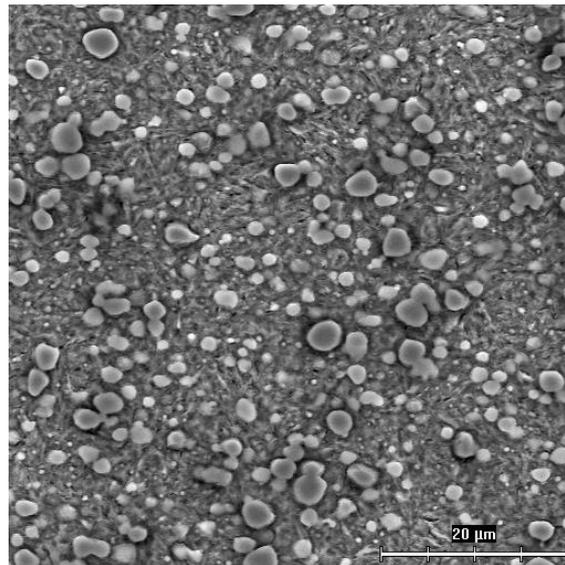
Heat treatment	Content of α' [%]	Content of γ_R [%]	Tetragonality of α'
Quenching	49.45	17.76	$c/a = 1.01186$
Quenching + SZ $-196^\circ\text{C} / 4 \text{ h}$	63.1	6.1	$c/a = 1.0223$



a)



b)



c)

Fig. 1. SEM micrographs showing the microstructure of Vanadis 6 steel in: as-quenched from a) 1000°C , b) 1075°C , c) 1075°C and 2x tempered at $530^\circ\text{C}/2 \text{ h}$.

Fig. 2 brings the hardness of the material as a function of both the T_A and the SZT. The as-quenched hardness is lower by 2 – 3 HRC than that after SZT, Fig. 2a. This can be explained simply by the fact that $(\gamma - \alpha')$ transformation was more completely finished due to SZT. Subsequent tempering led always to less or more significant hardness decrease compared to that of no SZT material, Fig. 2b. This was considered as surprising, however,

various authors [4, 15, 16] established and / or at least assumed that the SZT tends towards acceleration of phase transformations, which proceed in the steels during tempering and, as a result, lower as-tempered hardness of SZT steel can be expected.

Fig. 3 brings the σ_B as a function of T_A and SZT parameters. The σ_B decreases with increasing austenitizing temperature. It is a logical result of grain coarsening taking

place at higher T_A . The assessment of the effect of SZT on σ_B is more complex. For the material austenitized at 1000 °C, the σ_B was the highest when the steel was CHT and, with decreasing of SZT temperature and / or soaking time, the σ_B decreased. But, the σ_B became the best for the material SZT at -196°C/4 h when the austenitizing temperature was 1025 °C or higher. In addition, the σ_B was higher for the steel SZT at -196 °C / 10 h when austenitized at 1075 °C, also. From presented results, only those obtained on the samples austenitized at 1000 °C seems to be “logical”. One would say that the SZT

decreases material’s resistivity to crack initiation since more complete $\gamma - \alpha'$ transformation increases the surface roughness (effect of surface roughness on the σ_B was reported elsewhere [23]). But, the samples were ground before heat treatment so that the effect of surface roughness increase due to SZT can play only minor role. What is rather unclear is the opposite tendency of the σ_B at higher T_A . Here, several other factors should be considered: lower as-tempered matrix hardness of SZT material, resulting in higher fracture toughness [18] and higher plastic component of work of fracture [25].

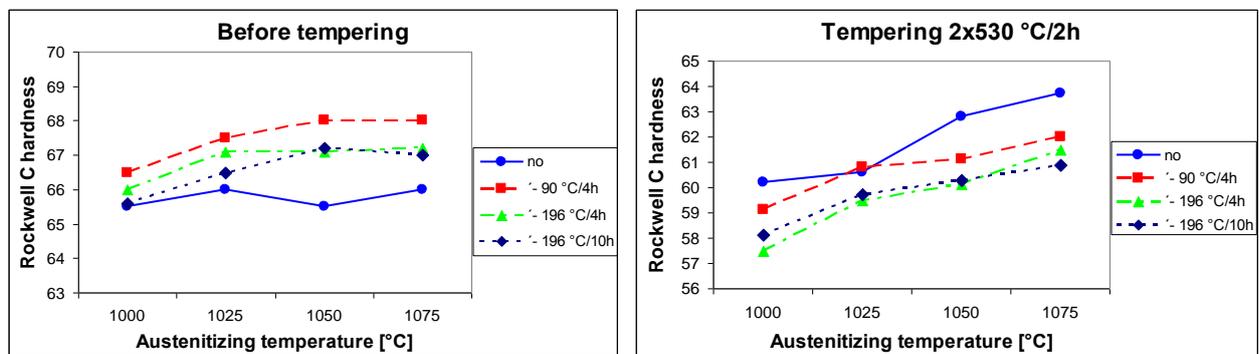


Fig. 2. As-quenched (a) and as-tempered (b) hardness of the steel as a function of austenitizing temperature and parameters of SZT.
(full colour version available online)

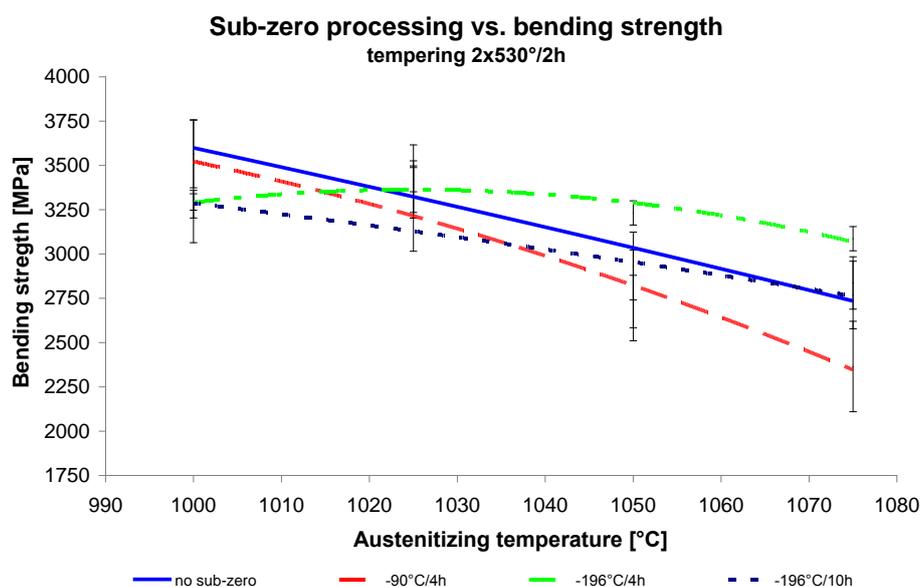


Fig. 3. Three point bending strength as a function of T_A and sub-zero processing.
(full colour version available online)

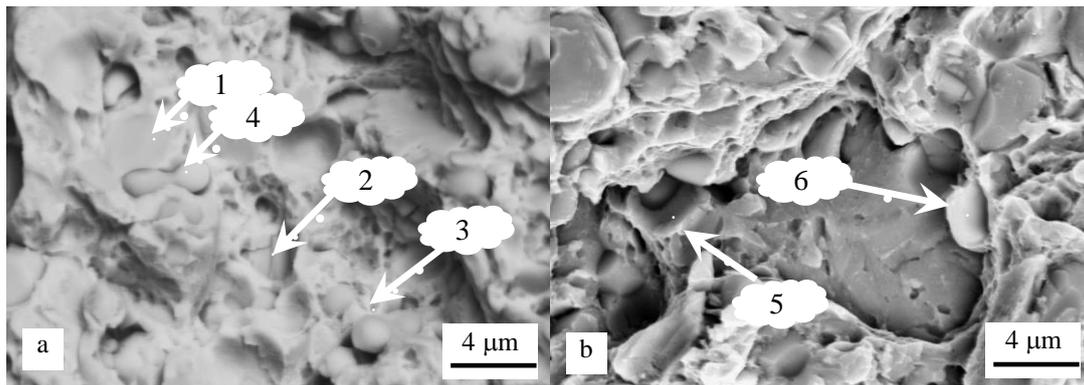


Fig. 4. Fracture surfaces of the specimens austenitized at 1075 °C. a – quenched and tempered, b – quenched, sub-zero processed at -196 °C / 4h and tempered. (1) – cleavage region in the matrix, (2), (3) – M_7C_3 – carbides, (4) – MC – carbides, (5) – decohesion at the matrix / carbide interface, (6) – M_7C_3 – carbides.

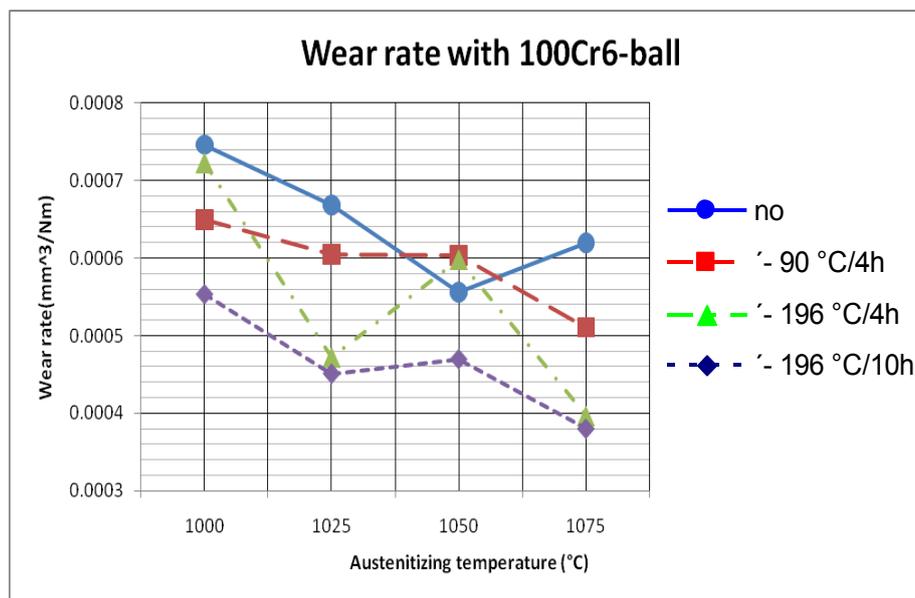


Fig. 5. Wear rate of the specimens made from Vanadis 6 steel and processed with different regimes. (full colour version available online)

Differences in the σ_B are reflected in the fracture surfaces, Fig. 4. The fractures were initiated at the tensile side of the testing specimens and they were propagated via several mechanisms. In the case of CHT material, Fig. 4a, the fracture surface exhibits clearly visible brittle cleavages (1). This cleavage mechanism of fracture propagation was accompanied with fragmentation of M_7C_3 -carbides (2,3) while the MC carbides remained almost unaffected (4). The fracture surface of the SZT steel, on the other hand, shows indications of plastic deformation of the matrix

(5), Fig. 4b. In this case, the fracture was propagated mainly by “dimple” mechanism, as a result of decohesion at the carbide / matrix interfaces (5). But, the fragmentation of M_7C_3 -carbides took place in the crack propagation, also (6).

Fig. 5 shows the wear rate of the Vanadis 6 steel after sliding against the 100Cr6 steel, as a function of the T_A and the parameters of SZT. Generally, the highest wear rate was recorded on the samples without SZT while the lowest ones were found when the material was SZT at -196 °C / 10 h. Effect of the

austenitizing temperature is clearly visible, also. The wear rate becomes lower with an increase of T_A .

The effect of T_A on the wear resistance is logical - increased austenitizing temperature results in hardness increase of ledeburitic steels.

The effect of SZT should be evaluated more complex. SZT steel has lower hardness than that CHT after the tempering regime used for the experiments. One can thus assume that the wear resistance of SZT Vanadis 6 steel should be worsened. But, the wear tests infer opposite tendency and, they are in line with other findings [5, 6, 15]. Das et al. [5, 9] have reported increased population density of small carbides due to SZT in as-low-tempered D2-steel. Also, our latest findings (not published yet) are consistent with those published by Das et al., e.g. sub-zero treated and no-tempered (this is a difference between our findings and those obtained by Das) Vanadis 6 steel contained enhanced population density of small, globular carbides (size less than 100 nm for the material austenitized at 1000 °C and less than 300 nm for that quenched from 1075 °C, respectively) compared to conventionally processed steel. Improvement in the wear resistance can be referred to following alterations in the microstructure: i – reduction of the volume fraction or almost complete removal of γ_R , ii – plastic deformation of virgin martensite connected with high dislocation density inside the martensite, iii – high internal stresses in the martensite (more complete $\gamma - \alpha'$ transformation), iv – formation of carbon clusters by means of capture the carbon atoms by moved dislocations whereas the clusters can serve as sites for subsequent carbides precipitation. Mentioned microstructural changes promote an acceleration of the precipitation phenomena in the α' and, as a result, the steel becomes slightly softer (overtempered) after tempering, carried out via the tempering regime standardly used for conventionally processed material, but without negative impact on the wear resistance.

4. Summary

The as-quenched microstructure of the Vanadis 6 consists of α' , γ_R and undissolved carbides. The amount of γ_R decreased with application of sub-zero treatment.

The as-quenched hardness is higher for SZT material. However, the as-tempered hardness of the SZT steel is lower than that of no SZT steel. Lower SZT temperature and/or longer processing time results in a further slight as-tempered hardness decrease. This could be due to microstructural changes in SZT steel, which promote an acceleration of phenomena taking place on tempering and, as a result, the steel becomes slightly overtempered when processed using a tempering regime recommended for conventionally heat treated material.

Three point bending strength of the Vanadis 6 steel is generally higher for samples SZT at -196°C for 4 h than that of the material processed at -90°C for 4 h or no-SZT steel. This is highlighted when higher temperature was applied for the austenitizing. Differences in three point bending strength are in line with the observations of fracture surfaces.

Wear resistance was improved via sub-zero processing. The lower the sub-zero processing temperature and / or soaking time, the better is the wear resistance.

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