

Simultaneous Improvement of Wear Performance and Toughness of Ledeburitic Tool Steels by Sub-Zero Treatment

Peter Jurčí, Jana Ptačinová, Mária Hudáková, Mária Dománková, Martin Kusý, Martin Sahul

Abstract—The strength, hardness, and toughness (ductility) are in strong conflict for the metallic materials. The only possibility how to make their simultaneous improvement is to provide the microstructural refinement, by cold deformation, and subsequent recrystallization. However, application of this kind of treatment is impossible for high-carbon high-alloyed ledeburitic tool steels. Alternatively, it has been demonstrated over the last few years that sub-zero treatment induces some microstructural changes in these materials, which might favourably influence their complex of mechanical properties. Commercially available PM ledeburitic steel Vanadis 6 has been used for the current investigations. The paper demonstrates that sub-zero treatment induces clear refinement of the martensite, reduces the amount of retained austenite, enhances the population density of fine carbides, and makes alterations in microstructural development that take place during tempering. As a consequence, the steel manifests improved wear resistance at higher toughness and fracture toughness. Based on the obtained results, the key question “can the wear performance be improved by sub-zero treatment simultaneously with toughness” can be answered by “definitely yes”.

Keywords—Ledeburitic tool steels, microstructure, sub-zero treatment, mechanical properties.

I. INTRODUCTION

MICROSTRUCTURE is the most important factor that governs the mechanical properties of steels. They are primarily influenced by carbon content, and through appropriate heat treatment. The strength and hardness increase with increasing the carbon content, but this increase results in loss in toughness, worsened ductility, and higher transient temperature. Also, the heat treatment that often consists of the austenitizing, quenching and tempering results in hardness (strength) increase but also in correspondingly worsened toughness, since soft ferrite/carbide microstructure is replaced by harder but more brittle martensite.

The only possibility how to increase the strength and ductility of steels simultaneously, albeit in certain limited extent, is a grain boundary strengthening induced by cold deformation and recrystallization. In this case, the yield stress σ is related to the grain size by the Hall-Petch equation [1]:

$$Df = Df_o + k * d^{-1/2} \quad (1)$$

where σ_o is a friction strain (it includes contributions from both the solutes and foreign particles), k is a constant, and d is the grain size being represented by the grain diameter.

Another example of simultaneous improvement of the strength and ductility is cold-drawn high-carbon steel wires. The strengthening effect is enabled by contemporary ferrite and cementite plastic deformation, which is connected with partial cementite decomposition and refinement of cementite lamellae [2], and can be described by “modified” Hall-Petch relationship [3]:

$$Df = Df_o + k * \exp\left(\frac{\epsilon}{4}\right) \quad (2)$$

where σ_o is the friction stress in the ferrite, k is a constant, and ϵ is the actual strain. At this place, it should be noted that the thickness of ferrite (or cementite) lamellae is inversely proportioned to the true strain [3], and it has to be determined experimentally, by quantitative metallography for instance.

High-carbon high-chromium (and vanadium) ledeburitic tool steels contain, apart from 1-2.5 wt.% C, also high amounts (typically 7-13%) of chromium, and up to 6 % of vanadium. These materials are used in many tooling applications where high hardness, superior wear resistance and good dimensional stability are required, e.g. fine blanking tools, powder compaction dies, cold forming of high-strength sheets, etc. Ledeburitic tool steels achieve their properties through appropriate heat treatment, which is specific for each steel grade. Generally, conventional heat treatment (CHT) consists of the austenitizing, quenching and double tempering. This procedure gives the steels a hardness of ~60 HRC, wear resistance, but makes the steels brittle and very prone to cracking when dynamically loaded for instance. Moreover, ledeburitic steels manufactured by classical ingot metallurgy suffer from poor and inhomogeneous carbide distribution; this makes an “extra” embrittlement of the materials and great level of anisotropy of mechanical properties [4]. Advanced PM ledeburitic steels do not manifest anisotropy of mechanical properties. Despite that, their toughness (being represented by three-point bending strength) is limited by approx. 3000 MPa, the fracture toughness is around 15-16 MPa.m^{1/2} [5], at a hardness of 60-61 HRC.

A simultaneous improvement of the hardness (wear resistance) and toughness of ledeburitic tool steels through either cold deformation or cold deformation with subsequent

Jana Ptačinová, Mária Hudáková, Mária Dománková, Martin Kusý, Martin Sahul are with the Faculty of Material Sciences and Technology of the STU in Trnava, Paulínská 16, 917 24 Trnava, Slovakia.

Peter Jurčí is with the Faculty of Material Sciences and Technology of the STU in Trnava, Paulínská 16, 917 24 Trnava, Slovakia (e-mail: p.jurci@seznam.cz).

recrystallization is impossible because of their high hardness, which is prerequisite for the use of tools. It is thus a great challenge for material scientists to find a way how to improve the toughness of commonly brittle steels, without a loss in wear resistance and strength.

The sub-zero treatment (SZT) is a supplementary process to the CHT, which is used for high-carbon and/or high-alloyed ledeburitic tool steels and bearing steels. These materials contain undesirable high amount of retained austenite after room temperature quenching. This phase is thermodynamically unstable, and can transform into brittle martensite when heavily loaded, for instance. As a result, undesirable dimensional changes of tools and components can occur, or these parts can fail as a result of crack initiation in newly formed “stress-induced” martensite. In SZT, the materials are immersed, immediately after quenching, into suitable cryo-processing media for pre-determined time and re-heated to a room temperature. The tempering brings the steels the final bulk hardness, tensile/compressive strength and the wear resistance.

The original purposes of the application of SZT were to reduce the retained austenite (γ_R) amount (increase the dimensional stability), and to improve the wear resistance. Careful measurements of the retained austenite amount, by X-ray diffraction, for instance clearly evidenced significant reduction of this phase in Cr SZT ledeburitic steels [6]-[14]. However, recent investigations clearly shown that the SZT also refines the martensite of these materials [6], [15], increases the population density of small globular carbides [7], [8], [12]-[14], [16], and tends towards acceleration of precipitation of transient carbides either during storage of the materials at a room temperature or slightly below, or during low temperature tempering [9], [17]. It is thus logical that these phenomena should make an overall microstructural refinement of ledeburitic steels, and one could thus expect a beneficial effect of SZT on toughness, apart from well known improvements in wear performance [8]-[12]. Hence, one of the main goals of the experimental efforts was to establish the opportunity to increase the wear resistance simultaneously with toughness, by using of proper combination of the SZT and tempering regime. A brief resume of the obtained results is the main objective of the current overview conference paper.

II. MATERIAL AND EXPERIMENTAL PROCEDURES

The experimental material was commercially available PM ledeburitic tool steel Vanadis 6 with a nominal composition (wt.%) of 2.1% C, 1.0% Si, 0.4% Mn, 6.8% Cr, 1.5% Mo, 5.4% V, and Fe as the balance. The initial state of the material was soft-annealed, with a nominal hardness of 284 HV 10, and the microstructure consisting of ferritic matrix, and uniformly distributed fine carbides, without any preferential orientation, Fig. 1. Apart from a relative simple chemical composition, this is why the Vanadis 6 steel has been chosen for the experimental purposes since the obtained experimental results clearly indicated that the orientation of semi-finished product can be disregarded in sampling [18].

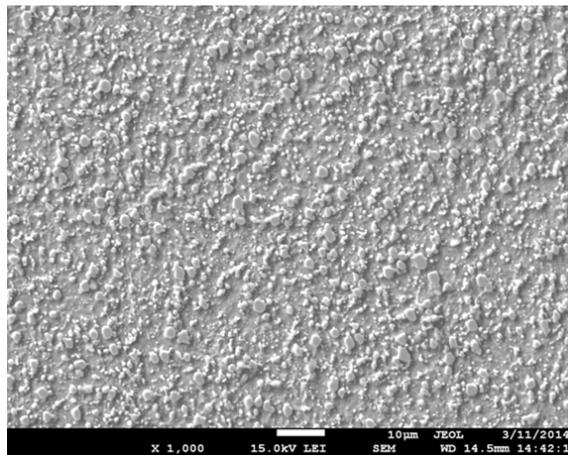


Fig. 1 SEM micrograph showing the microstructure of as-received Vanadis 6 steel

CHT consisted of the following steps: heating up to the desired austenitizing temperature of 1050 °C in a vacuum furnace, holding at that temperature for 30 min, and quenching by nitrogen gas (5 bar). One set of samples was processed without the insertion of SZT between quenching and tempering, while the other samples were subjected to SZT carried out at temperatures of -90, -140, and -196 °C, for different durations up to 48 h. Some specimens have been subjected to analyses in untempered state, in order to highlight the differences between CHT and SZT material, while others have been tempered. Double tempering (2 + 2 h) was performed at temperatures ranging from 100 to 600 °C.

- The following analyses have been carried out (the detail methodology can be seen in corresponding references):
- Qualitative and quantitative microstructural analysis by means of scanning electron microscopy and microanalysis [19].
- Microstructural analysis by transmission electron microscopy [20], [22].
- X-ray diffraction (qualitative analysis, determination of the retained austenite amount) [20], [21].
- Analysis of carbon atoms clustering at lattice defects, by means of internal friction measurements.
- Hardness measurements [20], determination of tempering diagrams [22].
- Determination of the flexural strength and fracture toughness [5], [21].
- Fracture analysis by SEM [5], [21].
- Determination of the wear performance [5].

III. RESULTS AND DISCUSSION

Fig. 2 is a series of SEM micrographs showing the microstructures developed by CHT, and by SZT at -196 °C with different durations. The matrix is martensitic with certain amount of retained austenite. The carbides are the eutectic ones (ECs), secondary carbides (SCs), and the small globular carbides (SGCs). Recent investigations have shown that the population density of both the ECs and SCs is invariant over

the heat treatment schedules used [20]. This is logical because the ECs are represented mainly by vanadium rich phase MC, which is stable up to almost the solidus temperature [19]. The SCs (based on chromium, M_7C_3) undergo dissolution in the austenite during heating up to a desired austenitizing temperature. However, the austenitizing temperature was kept

constant in the specimens whose microstructure is presented in Fig. 2, hence, it is logical that the level of the SCs dissolution will be the same. The population density of small globular carbides increases with the application of SZT. The maximum population density of these particles is developed when the duration of the SZT is 24 h, Fig. 3 (a).

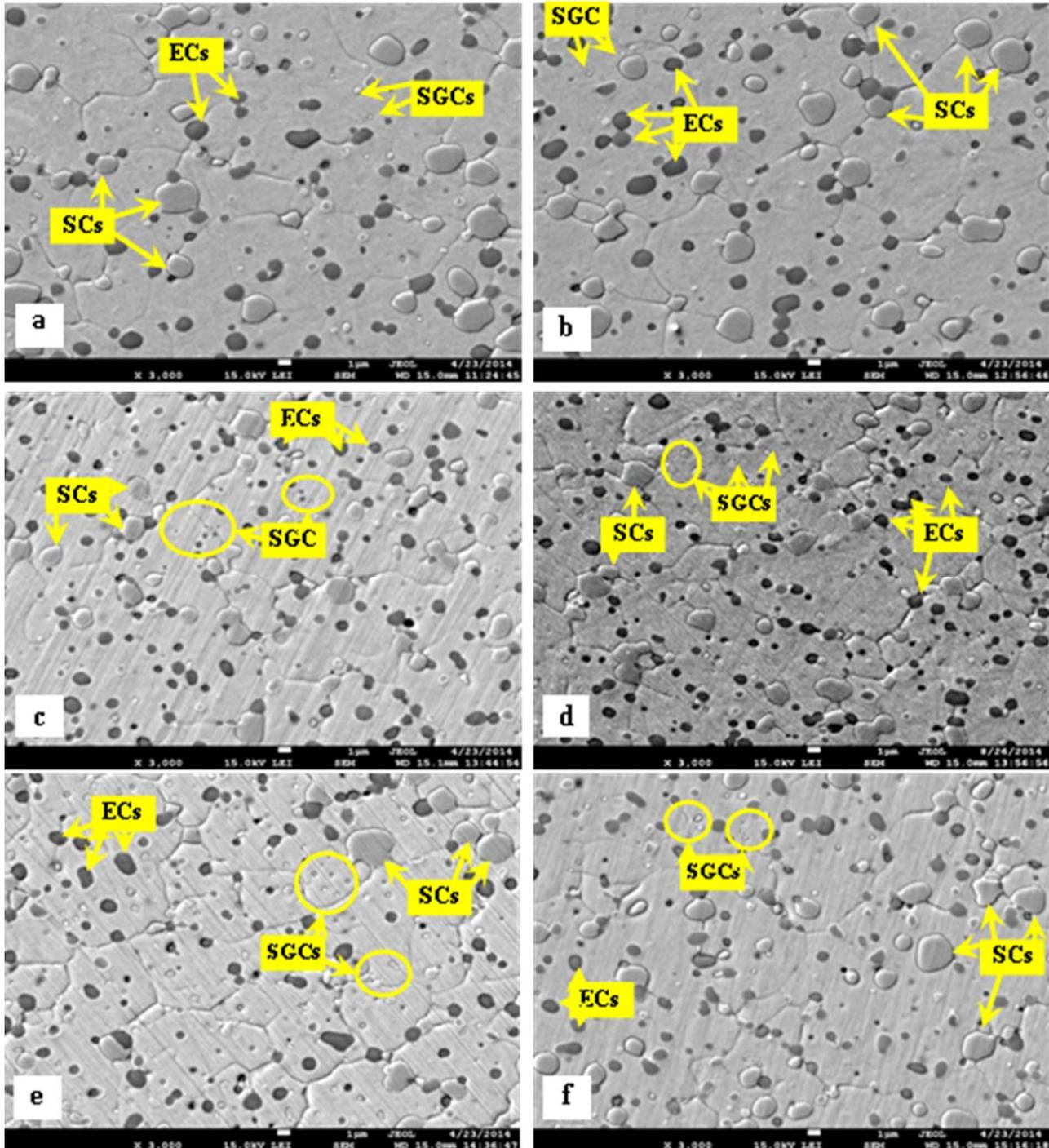


Fig. 2 SEM micrographs showing the microstructure of CHT Vanadis 6 steel (a), and the same steel after different durations of SZT, (b) 4 h, (c) 10 h, (d) 17 h, (e) 24 h, (f) 48 h

The amount of retained austenite in CHT material was 20.2 ± 1.6 vol.%, Fig. 3 (b). Application of SZT in liquid nitrogen reduces the retained austenite amount to 9.9 ± 1.6 , 2.9 ± 0.6 , 2.1 ± 0.5 , 2.9 ± 0.6 and 3.0 ± 0.7 vol.% for durations of SZT for 4, 10, 17, 24 and 48 h, respectively. Also, it is clearly shown that the variations in the population density of SGCs are closely related to changes in the retained austenite amount.

Recent TEM investigations led to the principal findings that the SGCs are cementite in their nature [20]. In addition, it has been found that the martensite of SZT samples is refined compared to what is formed in conventional room temperature quenching, Fig. 4.

In addition, thorough TEM investigations fixed nanosized cementitic particles within the martensite of SZT (for 17 h) Vanadis 6 steel, Fig. 5, [22]. These particles were located mainly at martensitic twins, inside the domains. It should be noted that no precipitates of fine cementite were observed in the Vanadis 6 steel that was not subjected to the SZT after room temperature quenching, and only carbon-rich and carbon-(almost) free sites were observed by HRTEM for SZT (for 4 h) Vanadis 6 steel [20]. Also, internal friction measurements confirmed that more interstitial carbon atoms are located at dislocation after SZT than after room temperature quenching, which act in favour of enhanced precipitation of transient phases.

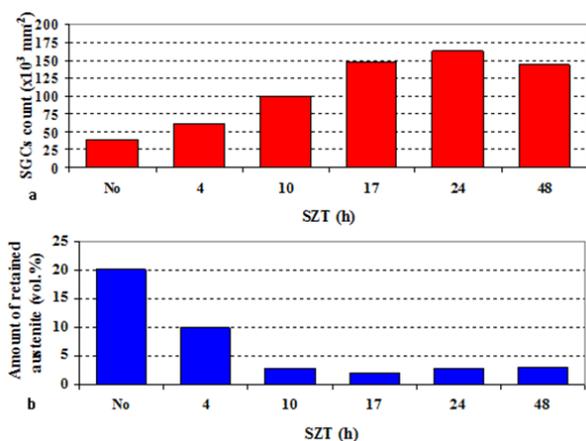


Fig. 3 Population density of SGCs (a) and retained austenite amount (b) for differently SZT samples of Vanadis 6 steel

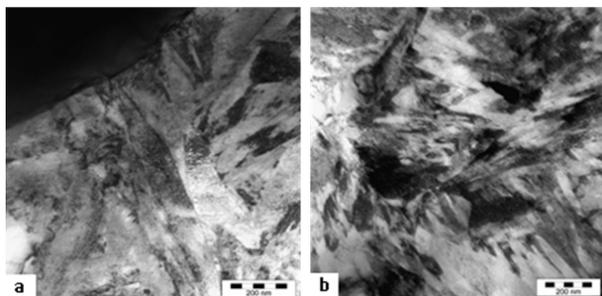


Fig. 4 TEM micrographs showing the microstructure of Vanadis 6 steel matrix after: (a) conventional quenching, (b) SZT [20] (adapted

from the corresponding reference)

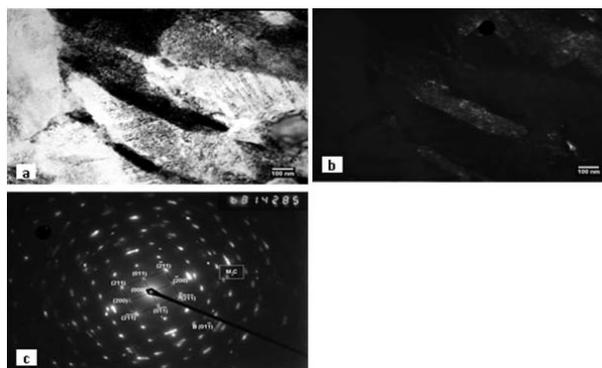


Fig. 5 Fine precipitates in SZT (with a duration of 17 h) Vanadis 6 steel, a) bright-field image, b) corresponding dark-field image, c) diffraction patterns of cementite [22] (adapted from the corresponding reference)

One can thus summarize that the microstructure of SZT ledeburitic tool steel Vanadis 6 differs from the conventionally room temperature one in the following aspects:

- i) Sub-zero treated material contains significantly reduced retained austenite amount, as a result of isothermal and time-dependent martensitic transformation, which takes place during the SZT.
- ii) The martensite of SZT steel is refined compared to that developed by conventional room temperature quenching.
- iii) SZT leads to clearly evident acceleration of precipitation of transient carbides during either the re-heating to the room temperature or short-term storage at the room temperature.
- iv) The last consequence of the SZT is considerably enhanced number and population density of small globular carbides (SGCs). The formation of the SGCs is time-dependent and follows well the reduction of the retained austenite amount.

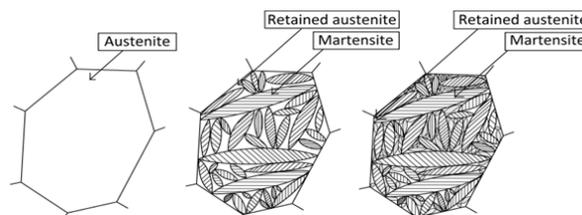


Fig. 6 A schematic of the microstructural development in the matrix, which takes place between the martensite start temperature and the end of the SZT

Mentioned differences between the microstructure of SZT Vanadis 6 steel and that developed by CHT originate from variations in microstructural development during the rapid cooling down to the room temperature, and that induced by the storage at the lowest temperature in the case of SZT.

First, it should be mentioned that during rapid cooling down, the matrix microstructure is fully austenitic at the moment when the characteristic martensite start temperature is

achieved, Fig. 6. The first martensitic domains grow relatively freely and fill up the original austenitic grains, up to a fraction that is determined mainly by the carbon content in conventional room temperature quenching. The martensitic transformation is connected with volume expansion; in the specific case of the Vanadis 6 steel, the volume change makes of around 3.1% [22]. Moreover, both the austenite and the martensite endure contraction during the cooling down, which is different for both phases due to clear difference in their thermal expansion coefficients [23]. As a result, compressive hydrostatic stresses are built up in the retained austenite [15], and the martensite is tensile strained.

Further cooling down, to the temperature of SZT, is the main driving force for the more complete γ to α' transformation. However, the formations of the γ_R are encapsulated between the martensitic domains formed in course of the CHT; this makes a spatial limitation for their growth during SZT, and they are finer than those developed during the room temperature quenching, as a consequence, see Fig. 6. Hydrostatic stresses, which are built up in the γ_R (note that these stresses exceed 1 GPa), hinder the further progress of the martensitic transformation effectively. Therefore, the only possibility to enable the further progress of the γ to α' transformation is the stress-induced formation of new phase,

which has higher specific density than the solid solutions. In the specific case of SZT Vanadis 6 steel, this phase was identified as alloyed cementite M_3C [20], [22], and this is the nature of "extra" SGCs that are formed during the isothermal hold at the cryotemperature. In other words, the formation of SGCs is a by-product of more completed martensitic transformation, according to (3). A schematic of the microstructural development between the room temperature quenching and the end of the SZT is in Fig. 7.



In contrast to the retained austenite, the newly formed martensite undergoes extensive plastic deformation during the SZT, which is connected with the capture of normally immobile carbon atoms by gliding dislocations, and their clustering at crystal defects. These clusters may either grow to or act as preferential sites for further carbide precipitation, as logically suggested by Meng et al., for instance [9]. This consideration, and also the findings by Li et al. [24], [25] are a logical explanation of accelerated precipitation rate of intermediate carbides in ledeburitic tool steels when they are subjected to the SZT.



Fig. 7 A schematic of the microstructural development between the room temperature quenching (a) and the end of the SZT (b), with particular attention to the formation of SGCs

Microstructural alterations due to the SZT are reflected in the hardness of the steel. As reported recently, the hardness of SZT material is enhanced compared to what was achieved by room temperature quenching, Fig. 8 [26].

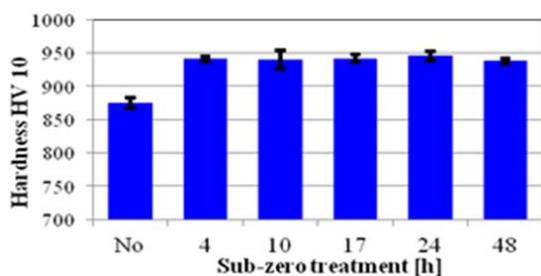


Fig. 8 Hardness of room temperature quenched and differently SZT Vanadis 6 steel. [26] (adapted from the corresponding reference)

Tempering induces decomposition of the retained austenite at high temperatures, which is faster in SZT material than that of CHT as shown in Fig. 9. This appears rather counterintuitive at the first glance; however, one can suggest that the retained austenite contains enhanced number of crystal defects after SZT, which may favour its faster decomposition. In addition, it is known that a stress relief may commence at temperatures above approx. 400 °C that may also act in favour of γ_R destabilization. And finally, the γ_R is depleted by carbon and alloying elements after application of SZT, due to formation of enhanced number of SGCs. This makes it more amenable to transformation, also.

Microstructural development of SZT Vanadis 6 steel during tempering is in Fig. 10. Irrespectively to the tempering temperature applied, the microstructure is composed of the matrix and carbides. These carbides are the ECs, SCs, and SGCs. The population density of both the ECs and the SCs is

not influenced by the tempering treatment. This is logical because the ECs are stable, theoretically up to the solidus temperature, and the amount of SCs can be changed only at much higher temperature, due to their dissolution in the austenite [19]. Alternatively, the population density of SGCs decreases with the tempering in SZT material, and this decrease is more pronounced at higher tempering temperatures, as clearly shown in Fig. 11. At this place it should be emphasised that despite significant decrease the population density of SGCs in SZT and tempered steel remains much higher than what can be obtained by CHT. Moreover, distinct microstructural changes take place within the matrix, and they are manifested by the presence of many nanosized, either regularly shaped or elongated particles, Fig. 10 (d).

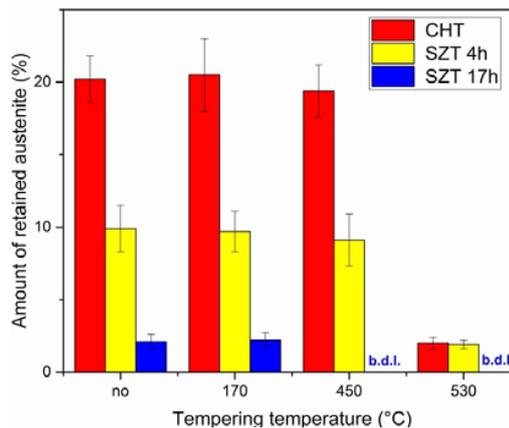


Fig. 9 Kinetics of the retained austenite decomposition for differently heat treated samples made of Vanadis 6 steel

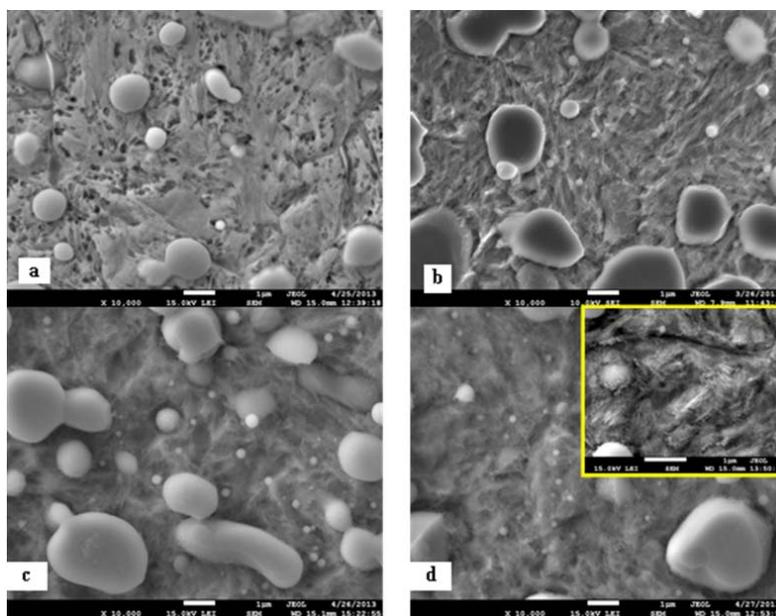


Fig. 10 Microstructural development that takes place during tempering of SZT Vanadis 6 steel (duration of SZT 4 h). (a) untempered, (b) tempering at 170 °C, (c) tempering at 370 °C, (d) tempering at 530 °C with detail of the microstructure recorded at high magnification

As discussed above, in the proposed model of the SGCs formation, see Figs. 7, enhanced population density of these particles in SZT material is a by-product of the isothermal martensitic transformation at the cryotemperature. It is known that tempering always reduces the thermodynamic instability of steels, which (apart from other phenomena) comprises a partial stress relief. The decrease in population density of SGCs can be then attributed to the stress relief during tempering. In addition, it has been determined in recent experimental work that the alloyed cementite (M_3C) is essentially metastable in the Vanadis 6 steel [27]; hence, it is prone to either dissolution or to transformation to more stable phases when thermally influenced.

The presence of nanosized particles in high-temperature tempered specimens can be attributed to the precipitation of carbides. The latest, yet not published results indicate that

these particles are special M_7C_3 carbides in conventionally quenched and tempered material while they are cementite in SZT steel. In the other words, the precipitation of special carbides, which normally proceeds at temperature of secondary hardening is suppressed due to the application of SZT.

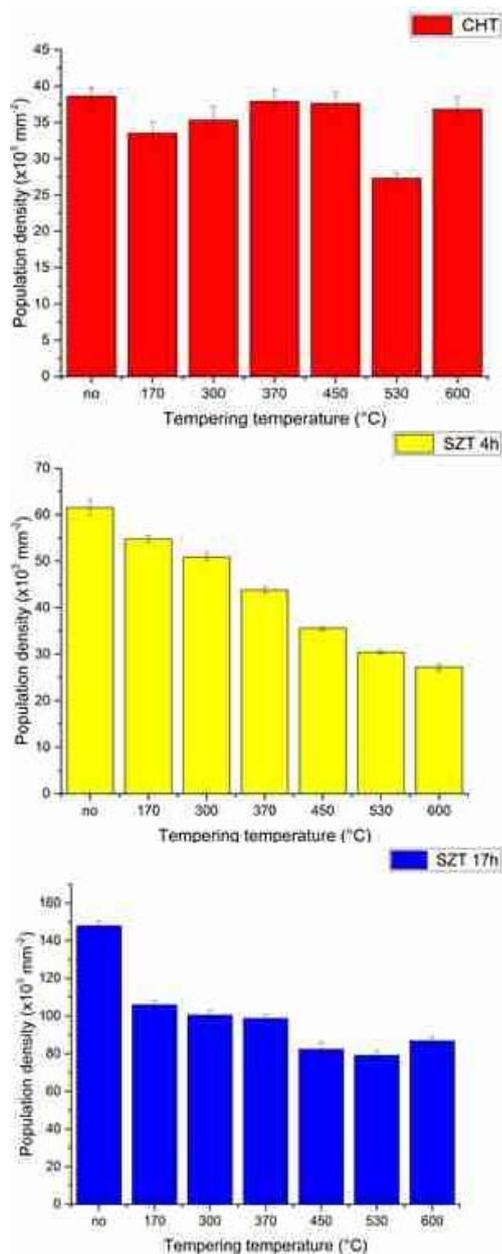


Fig. 11 Population density of SGCs in CHT and differently SZT Vanadis 6 steel, as a function of tempering temperature

The initial as-quenched (as-sub-zero treated) microstructures, and their changes that take place during tempering treatment have clear impact on the tempering response (and industrially important properties) of the materials. Higher martensite amount, correspondingly lower retained austenite amount, and much higher population density of SGCs make the steel harder but more brittle after tempering at low temperatures, see Figs. 12 and 13. Alternatively, the suppressed precipitation of special carbides, high-temperature softening of the martensite, and considerably limited transformation of retained austenite (note that the SZT steel is almost free of this phase, Fig. 3) make the steel slightly softer

when tempered within the normal secondary hardening temperature range. This makes the steel slightly softer (by ~ 30-50 HV 10, or 1-2 HRC), but, owing to retained enhancement in the population density of SGCs, much more wear resistant and tougher, Fig. 13. Finally it is worth noticing that similar results have been obtained for SZT and low-temperature tempered (around 200 °C) ledeburitic steels [7], [8], [10]-[13], [16].

IV. CONCLUSIONS

The application of SZT leads to considerable alterations in the microstructure of Cr- and Cr-V ledeburitic tool steels, i.e. to considerable reduction of retained austenite amount, refinement of the martensite, acceleration of precipitation rate of transient carbides at low temperatures, and to an enhancement of the number and population density of small globular carbides.

During the subsequent tempering, the precipitation of special alloy carbides is suppressed due to the SZT, the population density of small globular carbides decreases (but remains higher than after CHT), and the retained austenite undergoes decomposition at high tempering temperatures.

These microstructural changes manifest clear impact on industrially important properties of the steels that can be summarized as follows:

The hardness of the steels is higher due to the application of SZT, up to a certain "critical" tempering temperature; tempering at higher temperatures tends towards slightly lower as-tempered hardness.

Wear performance of high-temperature tempered steels is improved despite the hardness manifests rather slight decrease.

One should accept rather worsening of both the flexural strength and fracture toughness after low-temperature tempering. On the other hand, rather improvement in these characteristics can be expected after tempering within the temperature range of secondary hardening.

The answer to the key question "Can be the wear performance of ledeburitic steels improved simultaneously with their toughness" is "Definitely yes"; however, the extent of these ameliorations is not entirely determined yet.

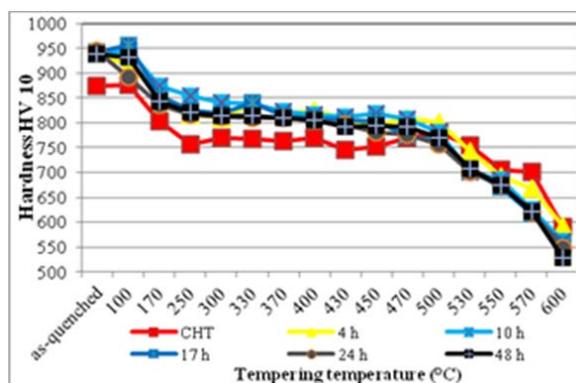


Fig. 12 Tempering diagram (hardness vs. tempering temperature) of CHT and differently SZT samples of the Vanadis 6 steel

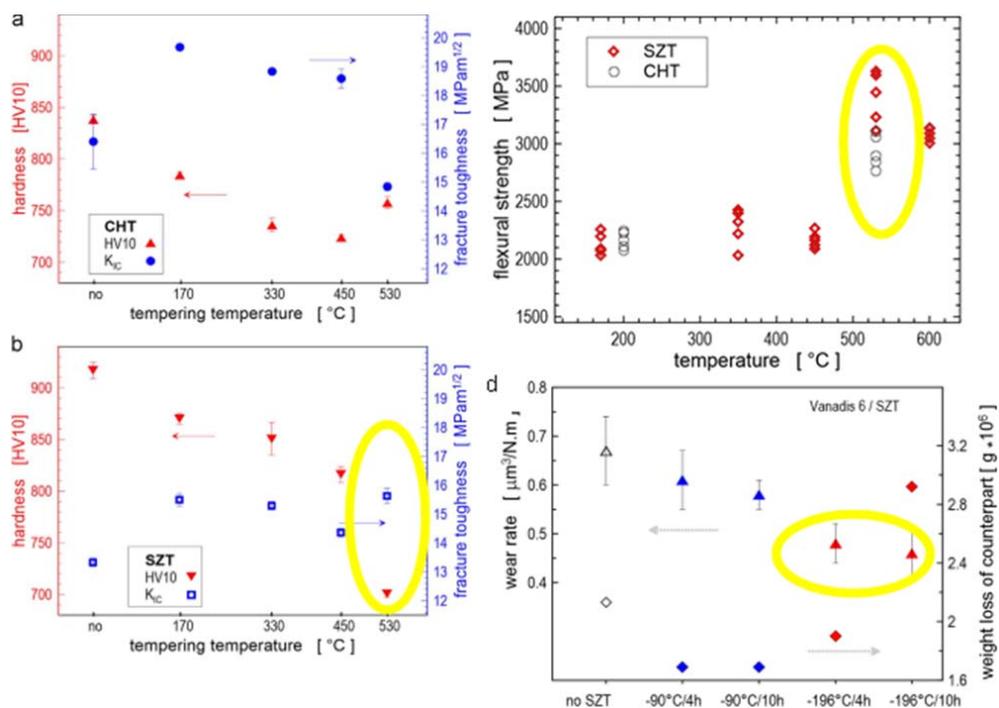


Fig. 13 Fracture toughness (a – conventionally quenched, b – SZT), flexural strength (c) and wear resistance (for the tempering temperature of 530 °C) of the Vanadis 6 steel [5], [21]. (adapted from the corresponding references). The temperature range of simultaneous enhancement of wear resistance and toughness is highlighted

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