MICROSTRUCTURAL CHANGES IN HIGH-ALLOYED TOOL STEELS BY SUB-ZERO TREATMENTS

MIKROSTRUKTURNE SPREMEMBE, NASTALE V MOČNO LEGIRANIH JEKLIH MED POSTOPKI PODHLAJEVANJA

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Recent investigations revealed and confirmed that sub-zero-treated ledeburitic steels differ from those after room-temperature quenching in four key aspects: 1) they contain considerably reduced amounts of retained austenite, 2) the martensite of sub-zero treated materials manifests clear refinement as compared with the same phase, but produced by room-temperature quenching, 3) a significantly enhanced number of small carbides (size 100–500 nm) is generated by sub-zero treatments, and iv) the accelerated precipitation rate of nano-sized transient carbides, resulting from sub-zero treatments was evidenced. The obtained results also indicate that the extent of these microstructural changes depends on the temperature and duration of sub-zero treatments, and that it is also material-dependent, i.e., the response of various steel grades to this kind of treatment differs considerably one from to another. A comprehensive overview of the impact of sub-zero treatments on the microstructural characteristics of various high-carbon and high-alloyed steels is the main topic of the current paper.

Keywords: high-carbon high-alloyed steels, sub-zero treatments, microstructure, martensite and retained austenite, carbides

Nedavne raziskave so pokazale in potrdile, da se s podhlajevanjem obdelana ledeburitna jekla razlikujejo od tistih, ki so po kaljenju ohlajena do sobne temperature, glede na štiri vidike: a) imajo bistveno manjšo vsebnost zaostalega austenita, b) martenzit podhlajenih jekel je bistveno bolj fini od martenzita, nastalega med kaljenjem do sobne temperature, 3) pomembno je povečana vsebnost drobnih karbidov velikosti od 100 nm do 500 nm, 4) pospešeno je izločanje karbidov nanometrične velikosti. Rezultati raziskav prav tako nakazujejo, da je obseg mikrostrukturnih sprememb odvisen od temperature in časa podhlajevanja in da je prav tako materialno odvisen; to pomeni, da se odgovor različnih vrst jekel na ta postopek močno razlikuje med seboj. V članku avtor podaja obširen literaturni pregled vpliva postopka podhlajevanja na mikrostrukturne lastnosti različnih vrst visoko ogljičnih močno legiranih jekel.

Ključne besede: visoko ogljična močno legirana jekla, postopki podhlajevanja, mikrostruktura, martenzit in zaostali austenit, karbidi

1 INTRODUCTION

The temperatures below room temperature, i.e., in the range 0 °C to –269 °C, are called cryogenic temperatures. These temperatures have been used to improve the wear resistance of tools and engineering parts over more than one hundred years. There are, for instance, stories of Swiss watchmakers who stored wear-resistant components in high-mountain caves, or experiences of old engine makers in the USA who employed the advantages of very cold winter time in the north of the country for the treatment of their engine blocks. Another example of the use of cryogenics in engineering dates back to the 1930s, when the German company Junkers used it for treatments of the components for the Jumo 1000-HP V12 aircraft engine.

In contrast to the long history and wide use of low temperatures in the treatment of metallic materials, the metallurgical background leading to this improvement became clear only over the past two decades. Up to the 1970s it was believed that the improvements in wear resistance caused by sub-zero treatments are only determined by a reduction of the retained austenite amount. Hence, the temperatures down to approx. –75 °C were accepted for the treatments within the professional community. Also, it has been recognized that direct soaking of the tools into containers with liquid nitrogen results in thermal shocks and failure of tools. This was why specialized heat-treating companies first dropped the idea of the use of lower sub-zero treatment temperatures.

Only much later was it found that the treatment at the temperature of boiling nitrogen further increases the performance of tools and components. This fact was demonstrated in real industrial applications like stamping, furniture manufacturing, powder compaction, sheet-metal forming, by using tools made of AISI D2 steel.[1]

As stated above, it was accepted up to end of 1970s that the ameliorations of some important properties, due to the application of sub-zero treatments, can be attributed to the reduction of retained austenite (γ_R) only, and that other possible mechanisms do not play a practical role. Only much later was it observed that sub-zero treatments enhance the amount and population density of

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carbides, refine the martensite, and modify the kinetics of the precipitation of transition carbides. The current paper presents an overview of the state of the art in understanding the processes that proceed in sub-zero treatments of high-carbon, high-alloyed tool steels.

2 MICROSTRUCTURAL CHANGES, THEIR DESCRIPTION AND DISCUSSION

The following text deals with the microstructural changes that occur during sub-zero treatments of high-carbon, high-alloyed tool steels. Changes in the retained austenite amount, the refinement of the martensitic structure, alterations in the carbide characteristics, and the impact of sub-zero treatments on the precipitation of nano-sized carbides during tempering will be presented and discussed.

2.1 Retained austenite

Table 1 shows the variations in the carbide percentage, matrix composition, and characteristic M_s temperature, as a function of the austenitizing temperature, for different chromium ledeburitic tool steels. It is obvious that the characteristic M_s temperature decreases with an increase of the austenitizing temperature, i.e., with increasing the level of carbides' dissolution in the austenite. The characteristic M_f temperature was not included in **Table 1**[2]; however, one can expect that it will be correspondingly lower than the M_s. This is supported by the results obtained by V. G. Gavriljuk et al.,[3] who found the temperatures of M_s and M_f to be 130 and –100 °C, respectively, for the steel X153CrMoV12 austenitized at 1080 °C.

Table 1: Volume percentage of carbides, contents of carbon and chromium in the matrix, and M_s temperature for differently austenitized chromium ledeburitic steels.[2] Note that the temperature of 1200 °C has not been used for the treatment of real industrial tools, and is given here as an example only.

Steel grade	Austenitizing (°C)	Carbides (vol.%)	Matrix composition (%)		Ms (°C)
			C	Cr	
X210Cr12	960	15.8	0.62	4.4	170
	1050	14.2	0.77	5.2	80
	1200	10.5	1.1	7.6	–120
X165CrMo V12	1050	12.6	0.58	4.9	160
	1200	6.8	1.08	7.8	–130
X155CrV Mo 12 1	1050	11.7	0.52	6.1	175
	1200	6.3	1.03	8.5	–100

There is great consistency within the scientific community in the claim that the γ_R is reduced due to the SZT because this fact was experimentally proved by many authors, and for different Cr and Cr-V ledeburitic tool steels.[4–13] An example of the X-ray patterns showing the reduction of intensity of characteristic peaks of retained austenite is presented in **Figure 1**.
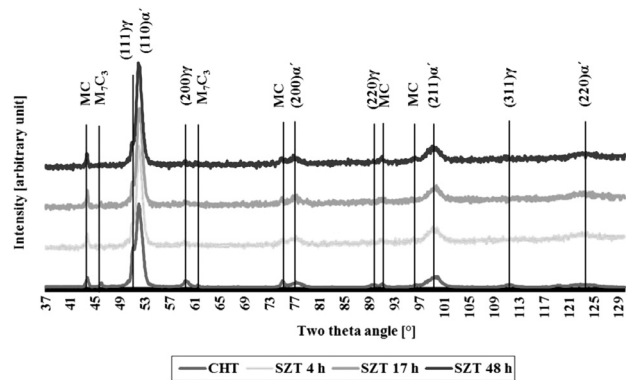

Figure 1: X-ray diffraction line profiles of CHT steel and steel after SZT at –140 °C for (4, 17 and 48) h

It can also be inferred from **Figure 2** that the retained austenite amount depends on the SZT temperature, and also on the duration of this treatment. In other words, the austenite-to-martensite transformation consists of two components. The first one is the athermal (diffusion-less) component, which takes place during the cooling of the materials to the lowest temperature of the heat-treatment cycle. The second component is the isothermal transformation that is active during the hold of the material at the cryotemperature. While the athermal component of the martensitic transformation is well known from the basic physical metallurgy of ferrous alloys, the presence of the isothermal component was first indicated by H. Berns,[2] and later reaffirmed by V. G. Gavriljuk et al.,[3] P. Jurči et al.,[5] D. Das et al.,[7] Tyshchenko et al.,[11] and by Villa, Hansen and Somers.[14] In addition, it was experimentally proved that the isothermal austenite-to-martensite transformation is the fastest at around –140 °C,[3,14] but rather lower temperatures should be used in order to maximize the extent of this transformation (or to minimize the amount of retained austenite).[5]

Even though very low temperatures (below the characteristic M_f temperature, sometimes also the temperature of boiling helium) are used for the SZT, and the treatment takes a very long time (mostly between 17 h and 36 h), the γ to α' transformation is never completed.
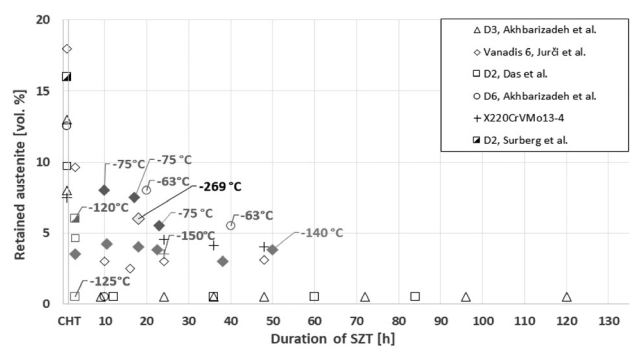

Figure 2: Amounts of retained austenite for various Cr- and Cr-V ledeburitic steels after different schedules of SZT (adapted from the corresponding references). Sub-zero treatment temperature was –196 °C, unless otherwise (by different colours and labels) indicated.
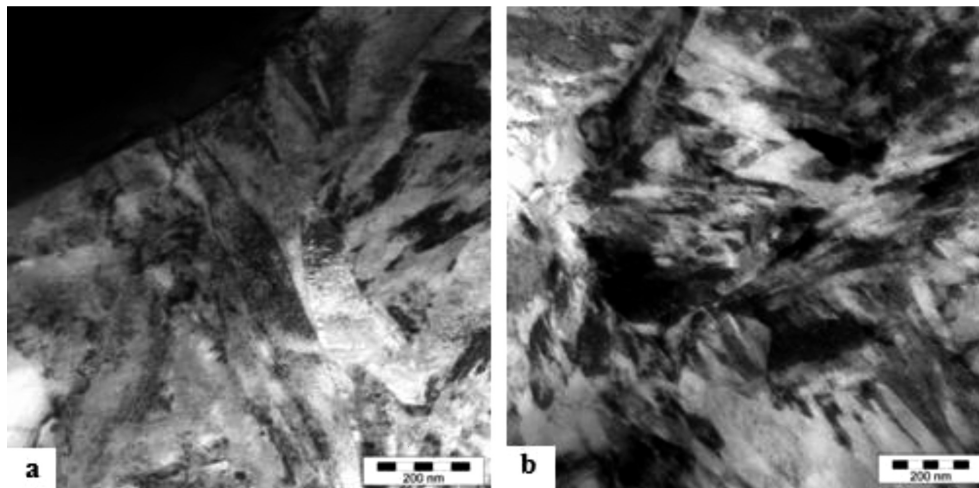
Figure 3: Bright-field TEM micrographs showing the matrix microstructure of Vanadis 6 steel after: a) conventional room-temperature quenching and b) after subsequent sub-zero treatment in liquid nitrogen for 4 h. Adapted from the [6]
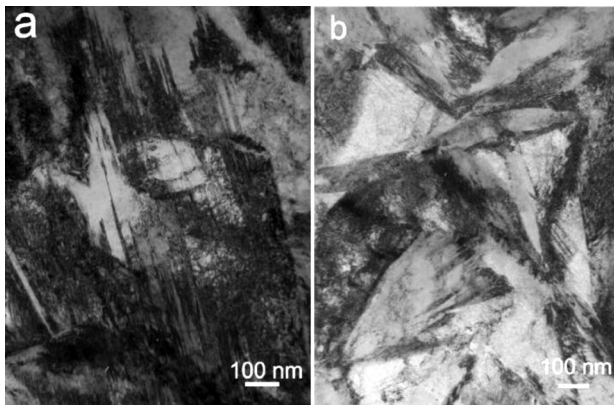

Figure 4: TEM micrographs showing the microstructure of martensite in steel X220CrVMo 13-4: a) as-quenched at room temperature and b) the same after subsequent holding at –150 °C for 24 h. Adapted from the [11]

The reason is that the transformation is connected with a volume expansion (martensite has a higher specific volume than the austenite). The increase in specific volume is directly proportional to the carbon content dissolved in the parent austenite,[15] and ranges between 2 % and 4 % in the case of high-carbon, high-alloyed steels. Last but not the least, it should be mentioned that a high state of compression is generated in the retained austenite by using the SZT.[16] As reported recently,[17] these stresses exceed 1500 MPa in Vanadis 6 steel after SZT at –140 °C. The state of compression in the retained austenite hinders the further progress of the martensitic transformation, despite the fact that the SZT temperature lies well below the characteristic M_f.

2.2 Martensite

The martensite formed at cryotemperatures manifests clearly evident refinement as compared with the same structural constituent developed by room-temperature quenching. Refinement of the martensitic domains has been reported by various authors, and for different
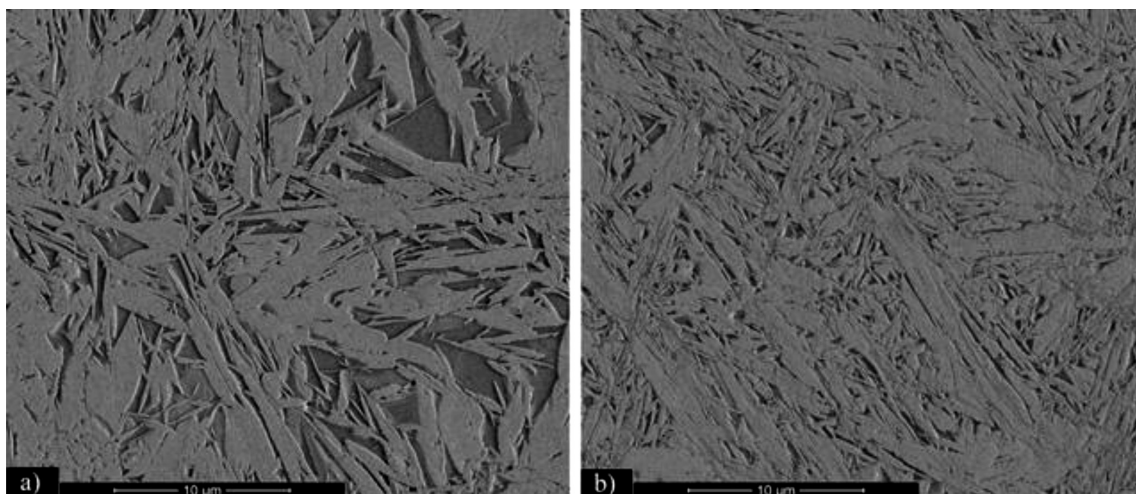

Figure 5: SEM back-scatter micrographs of AISI 52100 (100Cr6) steel austenitized at 1050 °C for 15 min, then quenched in oil at 140 °C, held there for 3 min: a) air cooled to room temperature and b) after additional sub-zero treatment at –170 °C for 7 h. Adapted from the [18]
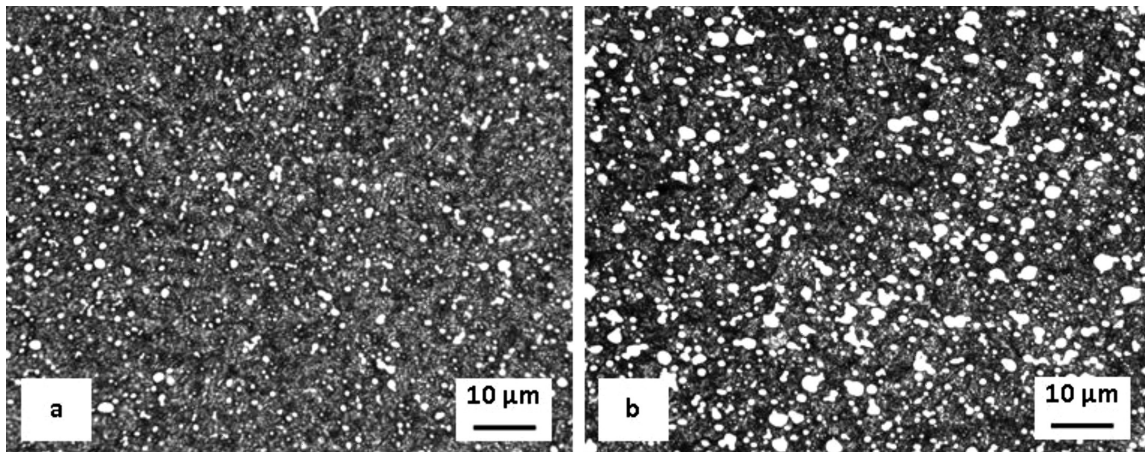
Figure 6: a) High-quality optical micrographs showing the microstructure of conventionally room-temperature quenched Vanadis 6 steel, and b) the same steel after subsequent sub-zero treatment at –196 °C for 17h. A Beraha-martensite agent was used for the etching. It is clearly visible here that the specimens differ in the number of carbides; however, an exact quantification of these particles is practically impossible.

high-carbon and ledeburitic steels.[6,11,17] Examples of the martensite refinement that resulted from sub-zero treatments are presented in **Figure 3**[6] for the Vanadis 6 steel, in **Figure 4**[11] for the steel X220CrVMo 13-4, and in **Figure 5**[18] for the steel grade AISI 52100. For the Vanadis 6 steel, the conventional heat treatment produces the martensite with a laths width typically in the range 50–80 nm, and laths length of around 500 nm. In contrast, SZT produces the laths width mostly between 20 nm and 40 nm, and a length of approx. one half of what was obtained by conventional room-temperature quenching.

A plausible explanation can be based on two phenomena. The first one is that the steel microstructure is fully austenitic before reaching the M_s temperature, thus the martensitic domains grow freely at the beginning of the transformation. In contrast, the material contains around 20 $x/\%$ of retained austenite after room-temperature quenching,[6] and austenitic formations are encapsulated within already-existing martensite. During the sub-zero treatment the further progress of the martensitic transformation takes place within these small austenitic formations, but the growth of the martensitic domains is limited by the size of the austenitic formations. The
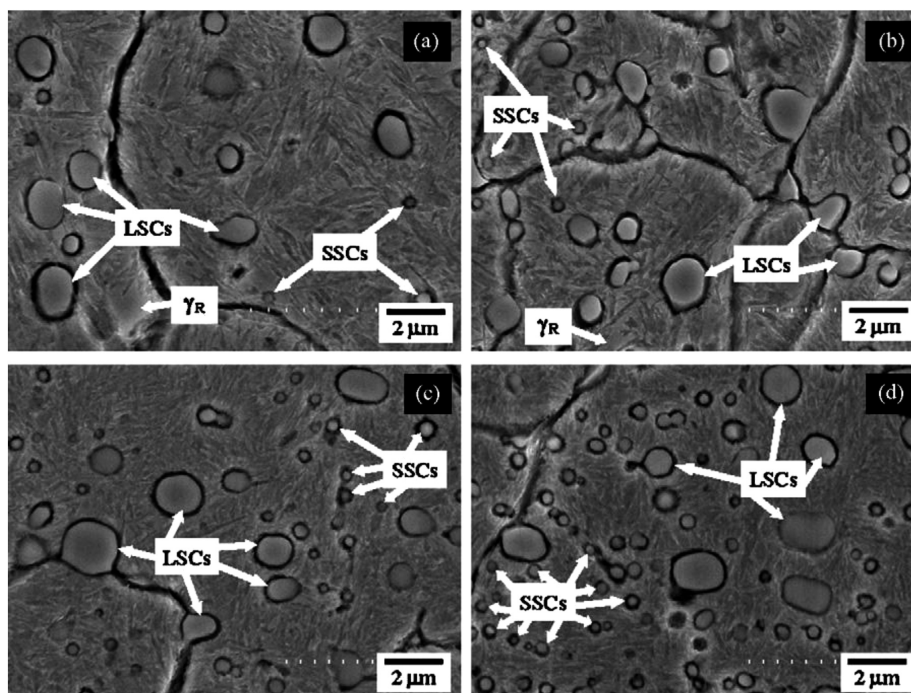

Figure 7: a) SEM micrographs showing the microstructure of conventionally heat-treated AISI D2 steel, b) the same steel after subsequent SZT at –75 °C for 5 min, c) after subsequent SZT at –125 °C for 5 min and d) after SZT at –196 °C for 36 h. Note that "large secondary carbides, LSCs" are actually secondary carbides (SCs), and that "small secondary carbides, SSCs" are actually not secondary phases, but they represent add-on carbides formed at cryotemperatures, as later presented and discussed. Adapted from [7]

second phenomenon responsible for martensite refinement can be introduced as follows. It has been proved earlier that not aged, but virgin, martensite is formed at cryotemperatures, e.g.[19,20] Virgin martensite is capable of deforming plastically (as reported by A. J. McEvily et al.[21] and J. Pietikainen,[22] for instance), which is reflected in a considerably enhanced density of the crystal defects within the martensitic domains.[5,6,11] In addition, plastic deformation is connected with the dislocation movement (albeit slow at low temperatures), and with the capture of carbon atoms with these dislocations. In other words, the isothermal part of the martensitic transformation is accompanied by mass transfer, which may be responsible for the growth of martensitic domains.

2.3 Carbide characteristics

In 1990s D. N. Collins[23] was the first who discovered the increase in the population density of carbides in differently sub-zero treated AISI D2 steel. Unfortunately, this investigator used conventional optical microscopy for the assessment, thus he missed many of the particles with a size that is below the detection limit of optical microscopes. Also, he did not differentiate between various carbide types (eutectic, secondary and others), hence, the reliability of the obtained results seems to be questionable. An example of the microstructures of Vanadis 6 steel acquired by conventional optical microscope is presented in **Figure 6**.

Much later, D. Das et al.[7,8] carried out a thorough analysis of the carbides in differently sub-zero treated AISI D2 steel, by using a scanning electron microscope (SEM), i.e., at much higher resolution than used by Collins. They arrived at the most principal findings, that the amount and population density of carbide particles increase with decreasing the temperature of sub-zero treatment, and that these characteristics manifest the maximum for SZT in liquid nitrogen with durations between 24 h and 36 h. The microstructures obtained in the referenced papers as well as the main results of the quantitative analyses of carbides are presented in **Figures 7** and **8**.[7]

They also suggested the mechanism responsible for the formation of add-on carbides, and they claimed that these particles are a result of the modified precipitation behaviour of carbide phases. In other words, D. Das et al.[7,8] assumed that a high-dislocation density is generated in martensite, due to the high internal stresses in the material resulting from the γ to α' transformation as well as from the fact that the martensite differs from the austenite in terms of thermal expansion coefficients. As a result, the martensite has a high thermodynamic instability, which results in the formation of carbon clusters near crystal defects. These clusters can either act as or grow into nuclei for the formation of carbides during subsequent tempering.

However, this theory does not bring a reliable explanation for the increased number and population density of carbides, as the latest experimental results inferred. The reasons for that are the following:

1) In Vanadis 6 steel, for instance, an increased population density of add-on carbides (small globular carbides, SGCs) was discovered already prior to tempering[6] (**Figure 9**), and the population density of these particles decreases with the application of tempering treatments, **Figure 10**. In addition, the number and population density of SGCs are time dependent, i.e., the duration of SZTs has an impact on them.[5,16,25] Moreover, the dependence of these carbide characteristics on the retained austenite amount obeys a high degree of correlation.[16]

2) It has been demonstrated that SGCs have a size ranging between 100 and 500 nm in most cases. For comparison, transient precipitates of either η- or ε-carbides formed at low tempering temperatures (up to 200 °C) are needle-like particles with a length of several tens of nanometers and much smaller width.[3,10] More stable cementite or M_7C_3 (the latest ones responsible for secondary hardening at approx. 500 °C) have similar dimensions.[5,6] Hence, one can thus only hardly imagine that regularly shaped particles with the above-mentioned size can be formed at very low temperatures by "classical" precipitation, i.e., by thermally activated transport of atoms.

3) Carbon atoms are immobile at temperatures around −100 °C and below,[3,11] hence, their segregation to nearby crystal defects by thermally activated transfer is unlikely. The only possibility to form carbon clusters is
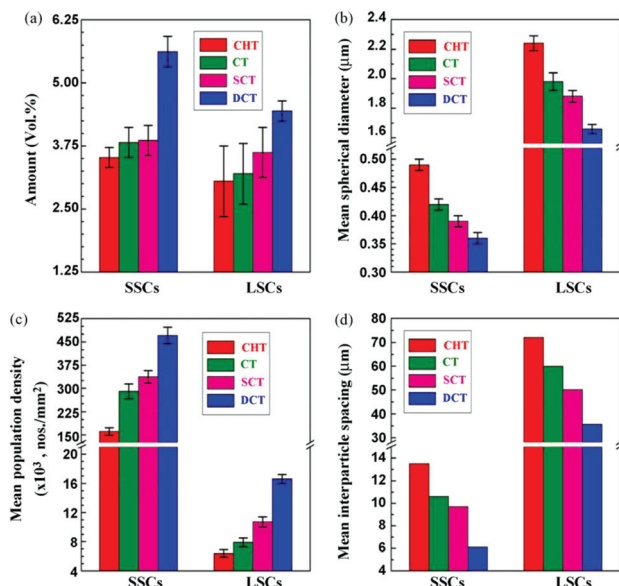
Figure 8: a) Image-analyses results for the amount, b) mean spherical diameter, c) mean population density, d) and mean interparticle spacing of carbide particles from **Figure 7**. Note that the carbides are denoted in the same way as in **Figure 7**. The symbols CHT, CT, SCT and DCT mean "conventionally heat treated", "cold treated" (actually −75 °C for 5 min), "shallow cryogenically treated" (actually −125 °C for 5 min), and "deep cryogenically treated" (−196 °C for 36h) steel, respectively. Adapted from [7]
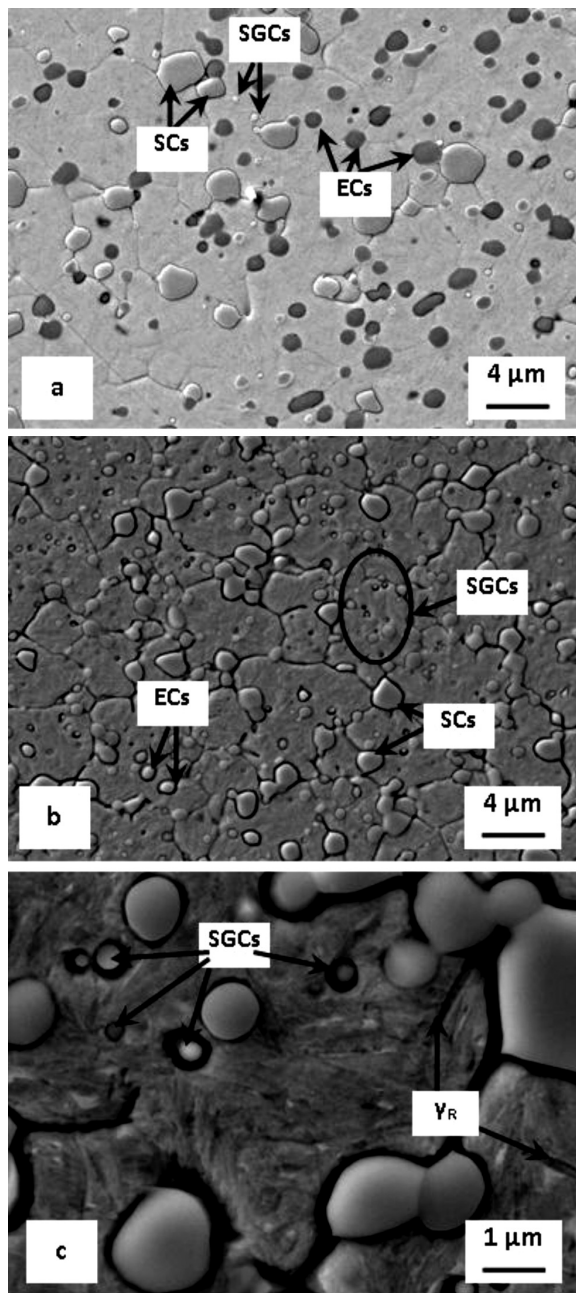
Figure 9: SEM micrographs showing the microstructure of conventionally room-temperature quenched Vanadis 6 steel (a), the same steel after subsequent sub-zero treatment at –140 °C for 17h, and a detail with particular attention to the matrix microstructure, (c).

thus their capture by moving dislocations, as a consequence of the plastic deformation of virgin martensite during the isothermal hold at the cryotemperature.

4) High compressive stresses are generated in the retained austenite.[16,17] These stresses hinder the further martensitic transformation, despite the strong driving force represented by the very low temperature. A close relationship between these stresses and the population density of SGCs has been discovered recently.[24]

Instead, a much more reliable theory can be proposed:

The state of high compression in the retained austenite hinders the further progress of the martensitic transformation, despite the temperature of SZTs lying well below the characteristic M_f temperature. The further progress of the γ to α' transformation, and the reduction of the retained austenite to a level of around 2 vol. % can only be possible when compressive stresses in the retained austenite would be reduced. The only possible way to reduce them is the formation of a phase with a lower specific volume than the major solid solutions. In a recent paper[6] it has been reported that the SGCs in the Vanadis 6 steel are of cementitic nature (M_3C – carbides). Also, it has been experimentally proven that the difference between the chemistry of the SGCs and matrix is minimal,[13] suggesting that no diffusion takes place in the formation of these particles. The density of the Vanadis 6 steel was determined to be 7505 kg/m³.[26] Among the relevant carbides, only cementite meets the criterion of a higher density than the martensite and the austenite; it was reported to be 7662 kg/m³.[27]

Therefore, the SGCs are considered as a by-product of the more complete γ to α' transformation, which takes place at cryogenic temperatures. Moreover, the formation of SGCs is stress-induced, rather than a result of the accelerated precipitation rate of the carbides on tempering.[5,28]

At the end of the current sub-section it is important to mention that the changes in the carbide characteristics take place in sub-zero treatments of only ledeburitic steels like AISI D2, AISI D3 or Vanadis 6,[6–9,16] and that these changes were not discovered in steels with near eutectoid or slightly hyper-eutectoid carbon content, like AISI 52110 steel.[17,18]

2.4 Precipitation of nano-sized carbides

In 1994, F. Meng et al.[10] were the first to challenge the postulate that the variations in the mechanical properties and wear resistance, caused by SZT, are attributed to only the reduction of retained austenite amount. They proved that SZT accelerates the
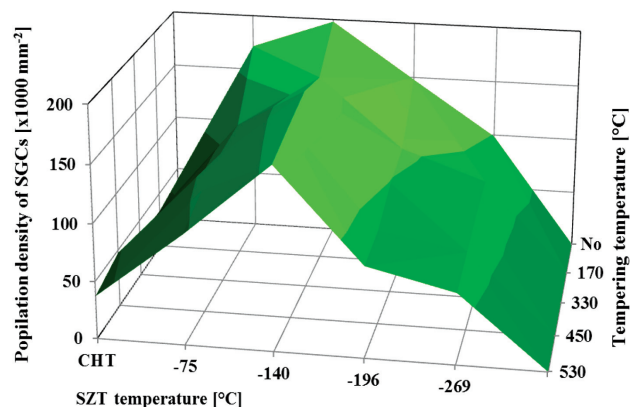

Figure 10: Population density of SGCs in the Vanadis 6 steel as a function of the SZT temperature (for a duration of 17 h) and tempering.
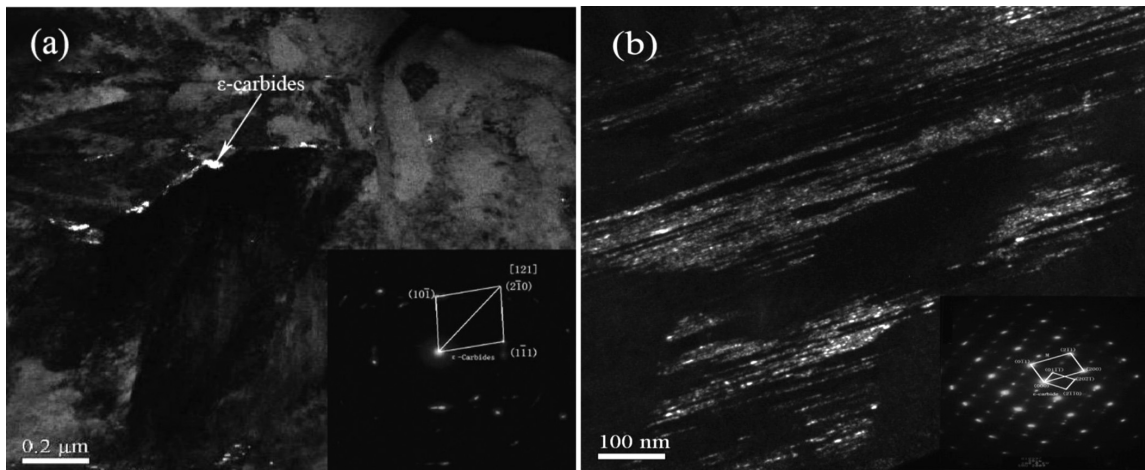
Figure 11: a) TEM images of ε-carbide in tempered martensite of sub-ledeburitic 8%Cr-0.9%C steel after austenitizing at 1030 °C, quenching and tempering at 210 °C for 2 h and b) after the same heat treatment, but treatment in liquid nitrogen with the duration of 40 h, was inserted in-between quenching and tempering. Adapted from the [29]

precipitation rate of nano-sized, transient η-carbides, thus to their higher number and makes a more uniform distribution in the AISI D2 steel. Much later, S. Li et al.[29] reaffirmed the finding on the accelerated precipitation rate of transient carbides, for sub-zero treated sub-ledeburitic 8%Cr-0.9%C steel. These results are displayed in **Figure 11**. It is shown that conventional room-temperature quenching followed by tempering at 210 °C results in the precipitation of a few particles of ε-carbide within the martensitic domains, **Figure 11a**, while the same tempering of SZT steel (–196 °C for 40 h) induces the precipitation of a huge number of fine ε-carbide particles within finely twinned martensite, **Figure 11b**.

In our recent investigations,[5,30] we have reported the enhanced precipitation rate of transient cementitic carbide in SZT Vanadis 6 steel. These results are very consistent with those obtained by Meng et al. and Li et al. **Figure 12** presents an example of the matrix micro-structure generated by sub-zero treatment at –140 °C, and for the duration of 17 h. The bright-field TEM image, **Figure 12a,** shows martensitic microstructure of the matrix, with a well-visible high dislocation density inside. The number of precipitates is relatively low, and the size of the particles is very small, in the range up to ten nanometers. Despite that it is sufficient for obtaining a dark-field image, **Figure 12b**. The analysis of the electron diffraction, **Figure 12c**, has disclosed that these particles are cementite.

However, the precipitation of transient carbides takes place only in the early stages of tempering treatment,[19,20] and often at tempering temperatures that are below the recommended values by steel manufacturers. At higher temperatures, these carbides transform to more stable phases, and thereby do not directly contribute to the changes in the mechanical properties of steels when tempered, for instance, within the secondary hardening temperature range. On the other hand, the precipitation

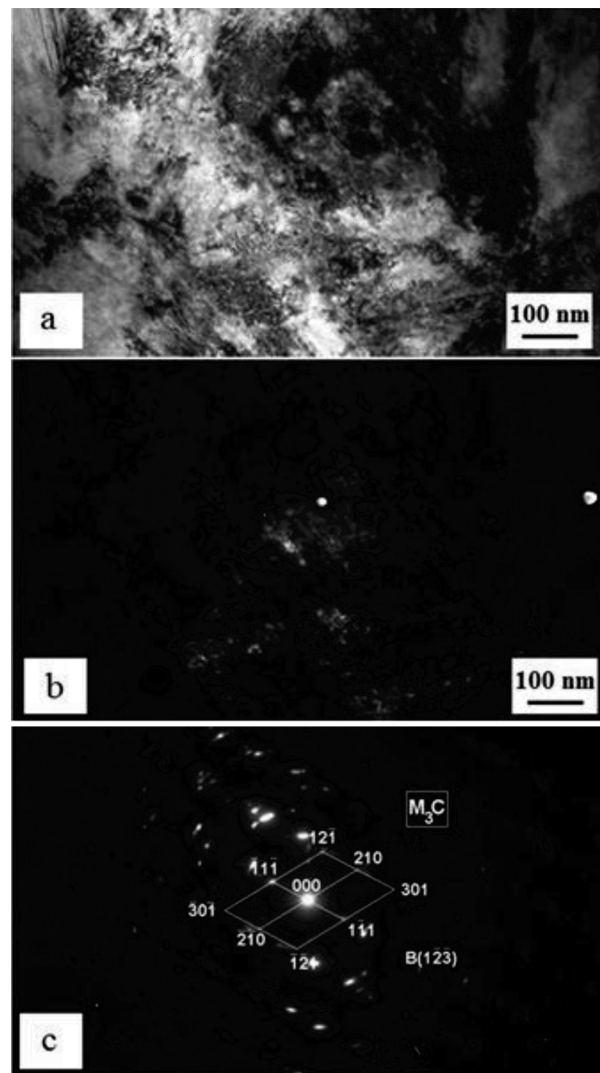

Figure 12: TEM micrographs showing the matrix microstructure of sub-zero treated (at –140 °C for 17 h) and no tempered Vanadis 6 steel: a) bright-field image, b) corresponding dark-field image, c) diffraction patterns of cementitic particles

of transient carbides can effectively increase the hardness, wear performance and durability of tools in selected cases, where low-temperature tempering is recommended, in particular.

At the end of the sub-section, a few words should be devoted to the changes in the carbide precipitation rate in high-carbon no-alloyed steels. However, the opinions on this matter are inconsistent to date. Eldis and Cohen, for instance reported the retardation of the first decomposition stages of the martensite (and precipitation of transient carbides at the same time)[19] while Villa et al. and M. Preciado and M. Pellizzari[17,31] either suggested or experimentally proved accelerated precipitation rate of these particles.

3 SUMMARY OF THE MICROSTRUCTURAL DEVELOPMENT

The following text summarizes the obtained results, and delineates presumable microstructural development in Cr and Cr-V ledeburitic tool steels when they are subjected to room-temperature quenching, followed by sub-zero treatment and tempering.

When cooling down from the austenitizing temperature, the matrix of the steel is fully austenitic before reaching the characteristic M_s temperature. Besides the austenite, the material contains certain amount of carbides, namely eutectic carbides (ECs) and a part of secondary carbides (SCs), **Figure 13a**.

At the beginning of further cooling down the martensite formations grow relatively freely, as there is no limitation for their growth within the original austenitic grains. However, continuously decreasing the specimen temperature leads to a progressively increasing amount of martensite, until the room temperature is reached. After the room temperature hardening, the matrix consists of the martensite and retained austenite, which is encapsulated in between the martensitic domains. The eutectic carbides and the secondary carbides are maintained in the material microstructure unaffected by the cooling, **Figure 13b**.

If the steel is immediately moved to the cryogenic system, the cooling continues. The martensite amount increases, but the growth of martensitic domains is limited by already-existing martensite, **Figure 13c**. This is the main source of the martensite refinement, as mentioned. above Because of volumetric effect of martensitic transformation the retained austenite is in high state of compression, which hinders the further growth of the martensite. On the other hand, the very low processing temperature is a strong driving force for further progress of the transformation. The only possible way how to enable the further conversion of the austenite to the martensite is a partial stress relief, through the formation of specific phases with a lower specific volume. This is why add-on small globular carbides are formed during the cryoprocessing, as **Figure 13c** illustrates.

The freshly formed (virgin) martensite formed at very low temperatures is able to undergo plastic deformation. The plastic deformation is connected with the dislocation movement, and with the capture of carbon atoms by gliding dislocations. These carbon atoms form clusters, which can act as nuclei for the precipitation of transient carbides. This is the principal explanation of why transient nano-sized carbides were identified in the steel after SZT and re-heating to the room temperature, **Figure 13d**, while these carbides were not discovered in room-temperature quenched steel. The mentioned carbon clustering also provides satisfactory answer to the question of why the precipitation of carbides is accelerated during the low-temperature tempering.

The tempering treatment induces partial stress relief in both the retained austenite and the martensite. Since the small globular carbides were formed at cryogenic temperature, under highly non-equilibrium circumstances, they are metastable and amenable to dissolute when thermally influenced, **Figure 13e**. This consideration is in line with experimental observations where the
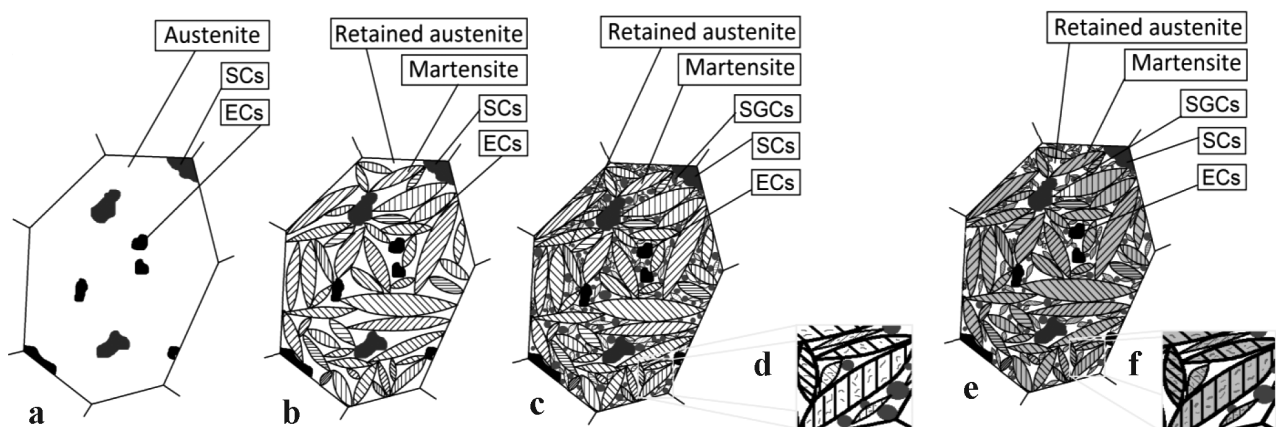

Figure 13: Schematic showing microstructural development in ledeburitic tool steels, which takes place during room temperature quenching, subsequent sub-zero treatment and tempering.

number and population density of add-on carbide particles decrease with tempering, and that the mentioned decrease is generally accepted phenomenon irrespective of the temperature of the sub-zero treatment or its duration.[5,13,30] The martensite undergoes decomposition during the tempering, which is manifested in its partial softening, and in further precipitation of nano-sized carbides. Some of these carbide particles coarsen while other particles transform into more stable phases, **Figure 13f**. In addition, the retained austenite decomposes during cooling down from the tempering temperature when the steel is tempered within common secondary hardening temperature range.

4 CONCLUSIONS

This overview paper deals with a summary of the latest experimental results, which were obtained by investigations of different high-carbon and high-alloyed steels when they were subjected to sub-zero treatments at different temperatures, and for different durations.

It can be stated that the most common effects of this kind of treatment are the reduction of the amount of retained austenite and the martensite refinement. An increased amount and population density of add-on (small globular) carbides is typical microstructural feature of sub-zero treated ledeburitic steels, while it is not present in near-eutectoid high-carbon non-alloyed steels. For most ledeburitic steels an enhanced precipitation rate of transient carbides was evidenced but, to date, the presence of this phenomenon was not convincingly proved for non-alloyed steels with near-eutectoid carbon content.

A plausible microstructural development of ledeburitic tool steels is delineated at the end of the paper.

Acknowledgements

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