IMPROVED PROPERTIES OF STEELS BY SUB-ZERO TREATMENT - CURRENT STATE OF UNDERSTANDING

JURČI Peter, PTAČINOVÁ Jana, HUDÁKOVÁ Mária, DOMÁNKOVÁ Mária

Faculty of Materials Sciences and Technology in Trnava, Slovakia, EU

Abstract

Favourable impact of sub-zero treatment on variety of important properties of tools is known over a long period. Alternatively, metallurgical principles responsible for elevated hardness, improved wear performance, changes in the tempering response and toughness, and better dimensional stability are known only over the last few years, and they have never been presented in all their complexity. The topic of the current paper is to make an overview of the most important properties of ledeburitic cold work die steels, their improvements by application of sub-zero treatments, and to explain these improvements upon the basis of the latest elaborated theory explaining the metallurgical background of this kind of treatment.

Keywords: Sub-zero treatment, retained austenite, martensite, carbides, mechanical properties

1. INTRODUCTION

The benefits of sub-zero treatment (SZT) on characteristics of high carbon high alloyed steels have been known for more than 150 years. Swiss watchmakers, for instance, have stored wear components in high mountain caves, in order to augment the wear resistance. In the middle of the 20th century it was commonly believed that temperatures down to approx. -79 °C are sufficient to transform high portion of retained austenite (γ_R) into the martensite (α´), and lower temperatures have no practical effect in treatment of steels. The effects like increased wear performance, improved fatigue strength, and better dimensional stability were accepted as the major advantages of SZT at these temperatures. Attempts to clarify the metallurgical background being responsible for the benefits of this kind of treatment developed only over the past two decades. This was due to the fact that the earlier state of the art of the experimental techniques was insufficient to record any changes in SZT and conventionally quenched (CQ) samples, and it was only believed that the changes in microstructure are at the atomic and nano-scale level. In the present paper, the state-of-the-art of understanding of metallurgical aspects that have the key impact on the most important structural features, and consequently on the properties of the steels is demonstrated.

2. CHANGES IN MICROSTRUCTURE

Conventional heat treatment of ledeburitic steels comprises heating up to the austenitizing temperature (T_A), hold at the temperature for time specific for each alloy, inert gas quenching, and two/three tempering cycles. As-quenched steels contain the α´, certain amount of the γ_R, and undissolved carbides. The γ_R is further transformed during subsequent tempering. This is coupled with precipitation of special alloy carbides. A so-called “secondary hardening” occurs due to complementary effects of these phenomena during tempering at around 500 °C. The saturation of the austenite with carbon and alloying elements lowers both the characteristic martensite start (M_s) and martensite finish (M_f) temperatures. The latter one can lie well below the room temperature. Hence, the CQ is insufficient to transform higher amount of the austenite into the martensite, which leads to unacceptable portion of γ_R in as-quenched steels. For more complete martensitic (γ - α´) transformation, a SZT can be inserted in-between quenching and tempering.

The first theory that attempted to explain the benefits of SZT was based on the reduction of the γ_R amount. It was assumed that lower amount of soft γ_R, and correspondingly higher fraction of α´ will lead to higher hardness and better wear performance. Many investigators really evidenced substantial decrease in γ_R amount due to SZT, **Figure 1** [1, 2, 3, 4, 5, 6, 7, 8].

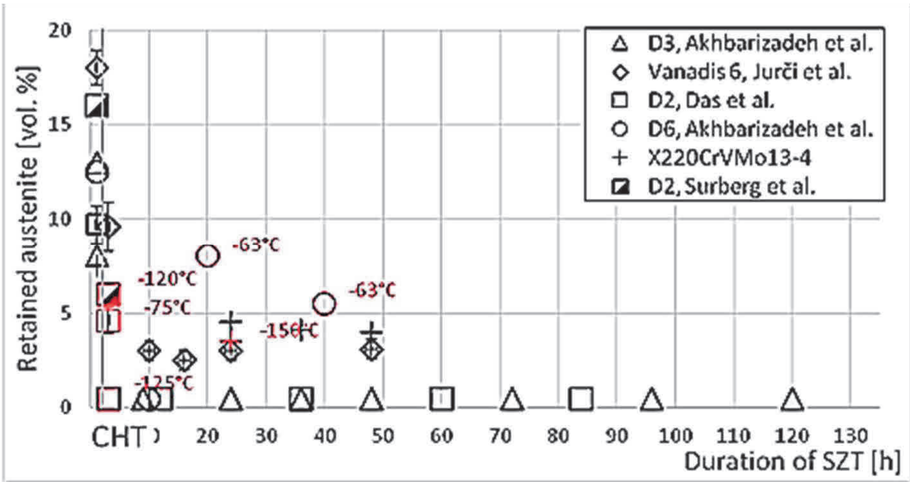

Figure 1 Amount of retained austenite for various Cr and Cr-V ledeburitic steels after different schedules of SZT [1, 2, 3, 4, 5, 6, 7, 8] (adapted from the corresponding references)

Later, this theory was challenged because it has been found that the material properties are further improved despite the γ_R was unchanged for longer SZT. Meng et al. [9], for instance, claimed that accelerated precipitation rate and better uniformity of transient carbides increases the wear performance rather than reduced γ_R amount. An example of precipitated transient carbides in SZT and untempered Vanadis 6 steel is in **Figure 2.** Other authors reported on enhanced population density of small globular carbides (SGCs, with a size 100 - 500 nm), see **Figure 3** as an example, and stated that these particles are responsible for much better wear performance [1, 2, 4, 5, 6, 10] along a relatively good toughness and fracture toughness [3, 10]. And finally, refinement of martensite due to SZT, see **Figure 4**, was also evidenced [1, 8, 11], and one can suggest its positive effect on some material properties, too.

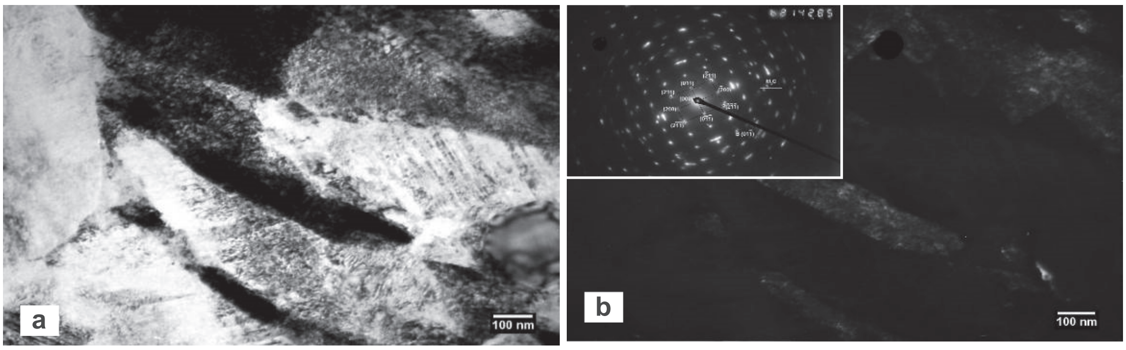

Figure 2 An example of fine precipitates, which were identified in SZT Vanadis 6 steel (note that these particles were not found in corresponding CQ material) [11] (adapted from the corresponding reference)

However, there were great inconsistences with regards to possible sources of mentioned microstructural features reported. Also, the thermodynamic aspects of mentioned phenomena are still under a great debate. For instance, some authors claim that the precipitation of transient nano-sized carbides is rather accelerated due to SZT [1, 9, 11] while others state that there is either no effect of SZT on the precipitation [12] or that the precipitation is retarded [13]. Also, enhanced population density of SGCs in SZT steels has been explained using implausible theories based on their accelerated precipitation rate during low-temperature tempering [2, 6]. These theories, however, can be easily challenged through commonly accepted facts that: i) carbon atoms are essentially immobile at low temperatures, hence, the probability of their segregation to nearby dislocations, where they form nuclei for further precipitation, is very low [8], ii) the size of SGCs is in the range of 100-500 nm, hence, it is thus unlikely that they can be formed during low-temperature tempering (between 150 and 220 °C) by thermally activated transport of atoms, iii) the SGCs were found already prior to tempering [1, 11], i.e. they are not a result of any tempering treatment but the SZT itself.

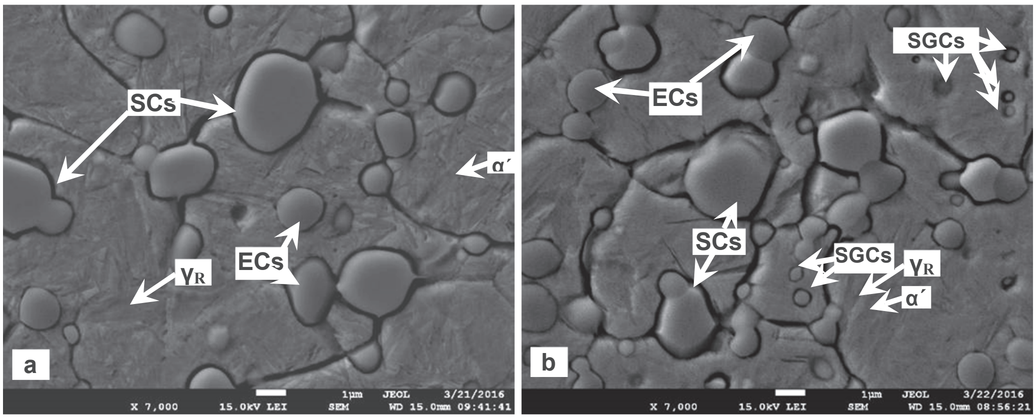

Figure 3 Example of different population density of SGCs in CQand SZT (for 17 h) Vanadis 6 steel

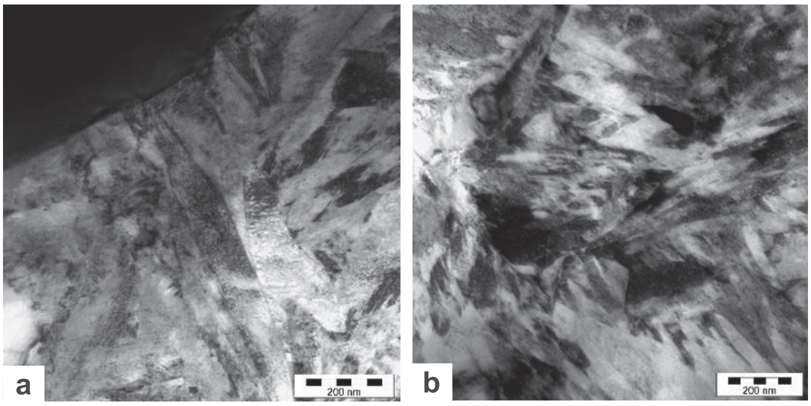

Figure 4 Comparison of TEM micrographs showing the microstructure of Vanadis 6 steel matrix after: a) conventional quenching, b) SZT [1] (adapted from the corresponding reference)

The current theory, which is elaborated based upon the latest findings, can be explained as follows:

First of all it should be noted that the aggregate γ_R to α´ transformation can be divided into two components [1]: i) diffusion-less (athermal) component, which takes place during cooling down from the T_A to the lowest temperature of the heat treatment cycle, and ii) time-dependent isothermal component, which is active during hold of the materials at a temperature of SZT.

The difference in γ_R amounts in CQ steels and the SZT ones makes ten or more per cents [1, 11]. It is generally accepted that the γ - α transformation is associated with 3 - 4% volume expansion. Moreover, both the martensite and the austenite endure considerable contraction during the cooling down to the lowest temperature of the heat treatment cycle, whereas they differ in terms of the extent of contraction due to significant difference in thermal expansion coefficient. As a result, compressive stresses are built up in the γ_R, and they increase with the application of SZT [14]. These phenomena result in the fact that the γ_R to α´ transformation is never completed despite the temperature of SZT lies well below the M_f temperature.

Alternatively, low temperature is a strong driving force for further progress of the transformation. However, this is only possible when the compressive stresses in the γ_R would be relieved, which can be realized through a deformation - induced formation of phase with lower specific volume. The obtained experimental data in the most recent investigations infer that [1, 11]: i) the increase in population density of SGCs is time - dependent, it follows the percentage reduction of γ_R [11], and these structural features manifest close relationship in terms of their percentage changes, ii) the nature of the SGCs was determined as cementite, i.e. as a phase with lower specific volume than that of the martensite or austenite, iii) the indications on plastic deformation of cementite particles were evidenced; it is expected that newly formed SGCs co-deform with the matrix during the isothermal part of the martensitic transformation. One can thus claim that the formation of SGCs is a “by-product” of the isothermal component of martensitic transformation, which takes place at the temperature of SZT.

Accelerated precipitation rate of transient carbides has been evidenced for different SZT steels either when low-temperature tempered [9] or already after re-heating to the room temperature [11]. Also, this phenomenon was only evidenced when the soaking time at the cryotemperature was sufficiently long [11, 15]. The explanation can be based upon the fact that the strain of the martensitic transformation is accommodated in the α´ and not in the γ_R. This accommodation is realized by slow but extensive plastic deformation of relatively ductile “virgin” martensite [16], which generates enhanced number of carbon clusters at crystal defects. These clusters can act as nuclei for further precipitation of carbides. It is worth noticing that the strained martensite is more amenable to decomposition as there is significant deviation from “standard thermodynamic conditions” claimed by Gavriljuk et al. [13], and supporting the theory on “delayed carbide precipitation”.

As described above certain amount of the austenite is transformed to the martensite during the hold at the cryotemperature. The phenomena associated with the isothermal γ to α´ transformation induce certain mass transfer, and might be responsible for controlling of the martensitic domains growth. Moreover, it has been demonstrated that the refinement of martensite is localized to certain sites in the microstructure while remaining volume fraction of the α´ does not manifest any refinement. It is obvious that the martensitic domains grow relatively freely during CQ (i.e. when only low amount of original austenite is transformed) but the space for the martensite growth becomes limited during the SZT since dominant austenite amount is already transformed. Hence, the domains of the martensite formed during the SZT would be finer.

3. EFFECT ON THE PROPERTIES

Enhanced hardness is generally accepted added value of SZT. The extent of as-SZT hardness increase depends on parameters of heat treatment schedule, and can range between several units [1, 2] and more than 10 HRC [17]. Improved hardness is retained after low-temperature tempering, also [2, 3, 4, 5, 6]. Mentioned hardness increase can be attributed to the lowered γ_R amount and correspondingly higher martensite amount, higher population density of SGCs, and to the accelerated precipitation of transient carbides. An opposite tendency has been recorded when the steels are tempered at temperatures from the secondary hardening range. The secondary hardening peak can either be shifted to lower tempering temperatures (for short-time SZT) [17] or it disappears completely when the steels are soaked in cryomedia for longer periods [10, 11]. The plausible explanation is based on reduced both the contribution of the secondary γ - α´ transformation and the precipitation of carbides. The first phenomenon is attributed to the much lower γ_R amount in SZT steels, and the second one can be referred to both the enhanced population density of SGCs and the accelerated precipitation rate of transient carbides, which essentially depletes the martensite prior to the precipitation of alloyed carbides at a secondary hardening temperature.

It is important that one should accept lower toughness and fracture toughness of SZT ledeburitic steels after low-temperature tempering. The deterioration is relatively high [3], and can be referred to reduced γ_R amount. Nevertheless, higher population density and better distribution of SGCs make serious obstacles in the crack propagation whereas the crack manifests a tendency to follow the carbide/matrix interfaces, which is associated with local microplastic deformation of a matrix [10]. This partly compensates negative impact of reduced γ_R amount. Alternatively, a beneficial effect of SZT on both the toughness and fracture toughness was recorded after high temperature tempering [10]. This is due to combined effect of slightly lower hardness and more favourable carbide characteristics as reported in [10, 11], for instance.

The first results on the prolonged durability of tools were obtained by practical testing, where an almost tenfold improvement in wear resistance of tools made of AISI D2 steel has been reported [18]. The results of laboratory tests carried out on differently heat treated Cr and Cr-V ledeburitic steels were in excellent agreement with the industrial trials. However, it was also established that the extent of improvements in wear performance is closely related to the duration of SZT [2, 4, 6], with a maximum at 36 h, and that it is load - dependent [4] and counterpart´s material nature dependent [10]. The current state-of-understanding is based on the more complete martensitic transformation, which induces formation of enhanced population density of SGCs. Moreover, these findings, along with those pertaining, the beneficial effect of SZT on toughness allow us to make a general conclusion that the application of SZT makes it possible to achieve a simultaneous enhancement in both the wear performance and toughness, albeit in a limited extent.

In the production of precision tools the dimensional stability is one of key properties that influence their durability. There is a general consensus with regard to the improvement of the material resistance against undesirable dimensional changes [7, 17]. It is known that conventionally room temperature quenched high carbon high alloyed tool steels contain around 20 vol. % of γ_R. This phase is metastable at low temperatures and can transform to brittle martensite under high mechanical stresses. As discussed above, the γ - α' transformation is associated with positive volume change, which is responsible for undesirable dimensional changes of heavily stressed components containing too high γ_R amount. Therefore it is commonly accepted that the amelioration of dimensional stability can be simply referred to the reduction of the γ_R amount.

The dominant amount of tools made of Cr and Cr-V ledeburitic steels is used in environments where corrosion resistance does not play crucial role in their service time. However, experimental results indicated on worsened corrosion resistance due to the SZT [19], which is related to higher population density of SGCs that depletes the solid solutions by carbon and alloying elements.

4. CONCLUDING REMARKS AND PRACTICAL RECOMMENDATIONS

Sub-zero treatment leads to considerable reduction of retained austenite amount, which takes place mainly during isothermal hold at the cryotemperture. This is associated with development of high compressive stresses in this phase, and with extensive plastic deformation of newly formed “virgin” martensite.

Low-temperature isothermal martensitic transformation induces “secondary effects” like enhanced precipitation rate of transient carbides, formation of extra SGCs, and overall microstructural refinement.

These phenomena result in general hardness increase of SZT steels, which is evidenced up to a critical tempering temperature, loss of the secondary hardening, better wear resistance and dimensional stability, and changes in toughness and fracture toughness. Also, it seems that it is possible to increase the wear performance and toughness simultaneously, by using a proper heat treatment route.

The following practical recommendations can be derived from the obtained results: If the goal of the heat treatment is to achieve the maximal hardness and wear resistance, the use of higher T_A is desired. In this case, higher retained austenite amount is almost fully converted to martensite by SZT, which should maximize the population density of carbides. A low-temperature tempering must be carried out subsequently. In this case, however, lower toughness must be inevitably accepted. If the tempering to secondary hardness peak is used in the heat treatment schedule then the wear performance is also improved, however, the improvement is less significant. A slight improvement in toughness is undisputed benefit of this schedule. The lowest possible amount of retained austenite should be achieved if the objective is to minimize the dimensional changes. This means the use of low T_A along with sufficient duration of the SZT.

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