PHASE CONSTITUTION OF SUB-ZERO TREATED VANADIS 6 TOOL STEEL

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Abstract

The microstructure of sub-zero treated Vanadis 6 tool steel has been examined with reference to the same material without the application of sub-zero treatment. Changes in the microstructure were recorded using light microscopy, scanning electron microscopy and transmission electron microscopy. The obtained results infer that the amount of retained austenite decreases with application of sub-zero treatment. The retained austenite is located mainly along the boundaries of martensitic domains. The martensite is refined due to sub-zero treatment. The carbide phases in as-quenched and/or sub-zero treated Vanadis 6 steel can be divided into eutectic phases (MC-carbides), secondary carbides (M_7C_3-phase) and small globular carbides that were identified as alloyed cementite. Sub-zero treatment refines the carbides and increases their number, particularly the small globular carbides, but it does not alter their nature. It is hypothesised that the amount of small globular carbides is enhanced due to extensive stress state of the material after SZT rather than as a result of "accelerated precipitation rate" that was considered recently as a principal explanation.

Keywords: Ledeburitic tool steel, sub-zero treatment, microstructure, phase constitution, hardness

1. INTRODUCTION

Sub-zero treatment (SZT) has been accepted as a method how to reduce the amount of retained austenite (γ_R), which can have detrimental effect on the service life of tools made of Cr- and Cr-V ledeburitic tool steels and thereby to improve several properties of tools since 1st half of 20th century. The attempts pertaining to the clarification of metallurgical background being responsible for these improvements are much younger, however. In first theories it was believed that the reduction of γ_R is the key factor being responsible for ameliorations of their performance. Later investigations arrived to opposite findings, e.g. the ameliorations in wear resistance, hardness and other relevant properties are based on completely other mechanisms.

Meng et al. [1] have reported on accelerated precipitation rate and better uniformity of intermediate η - carbides due to the SZT of AISI D2 steel and they believed that this contributes to the wear resistance rather than lowering of the amount of γ_R. Collins [2] has established an increased population density of carbides (with a size < 5 μm) in sub-zero treated AISI D2 steel. He has used an optical microscope for the investigations, thus, he has surely missed the particles that have been reported by Meng et al. [1]. Despite that, they claimed that the wear resistance of the material was improved due to presence of carbides having a size < 5 μm, e.g. their claims are in clear discrepancy to the Meng´s ones. Recent investigations made by Das et al. [3, 4] and Akhbarizadeh et al. [5, 6], carried out on the AISI D2, AISI D3 and AISI D6 steels, respectively, by using the scanning electron microscopy, confirmed that irrespectively to the steel grade, the percentage of small globular carbides (SGCs) with a size less than 0.5 μm increases due to the SZT.

In our latest paper [7] it has been demonstrated that the martensite formed during SZT of Vanadis 6 steel (-196 °C/4 h) is refined compared to that produced by conventional quenching, it manifests higher dislocation density and contains carbon-rich and carbon-depleted areas. The microstructure of the steel contains enhanced number of SGCs (size of around 100 nm). Their nature was determined as cementite. Investigations have revealed that SZT does not alter the nature of SGCs but only their amount. Finally it was found that SZT in liquid nitrogen for 4 h reduces the amount of γ_R by few percents when low austenitizing temperature was

used while the reduction of γ_R was twice and more when higher austenitizing temperature was used for the treatment.

Literature review shows that despite great number of studies devoted to the investigation of the effect of SZT on different materials, a considerable amount of differences is evident in the obtained results and theories attempting to clarify these results. This partial study is focused to investigation of the effect of sub-zero treatment in liquid nitrogen on the microstructure and hardness of Vanadis 6 cold work die steel and to attempt and hypothesise some phenomena taking place in sub-zero treatment.

2.   EXPERIMENTAL PROCEDURE

A PM tool steel Vanadis 6 with nominal chemical composition (wt. %) 2.1 C, 1.0 Si, 0.4 Mn, 6.8 Cr, 1.5 Mo, 5.4 V and Fe as a balance has been used for investigations. Specimens were divided into separate batches and subjected to conventional quenching and SZT in liquid nitrogen (-196 °C) with a duration of 17 h. In conventional quenching, the specimens were gradually heated in vacuum furnace, up to the austenitizing temperature of 1050 °C with a hold at the temperature for 30 min and nitrogen gas quenched to a room temperature. Sub-zero treatments were done immediately after quenching. In these treatments, conventionally quenched specimens were cooled down slowly (1°C/min) from room temperature to the temperature of liquid nitrogen, held there and heated up to the room temperature at a heating rate of 1 °C/min. Subsequently, the samples were double tempered at temperatures from the range 100 - 600 °C.

Microstructural investigations were completed using light microscopy, scanning- (SEM) and transmission electron microscopy (TEM). For the SEM, a JEOL JSM 7600F apparatus, equipped with an EDS-detector Oxford Instruments, was used. The microstructure was recorded in mixed detection regime (MDR), consisting of 50 % of secondary electrons (SE) and 50% of backscattered electrons (BE). For the TEM, a JEOL 200CX apparatus operating at an acceleration voltage of 200 kV was used. Quantitative analysis of carbides was carried out following the recent findings [8] and the details were described in [7]. Twenty five micrographs were considered for each specimen in order to ensure the statistical reliability associated with these investigations. Content of the γ_R was measured by X-ray diffraction analyses of the bulk specimens, using a PHILLIPS PW 1710 apparatus with filtered Co$_{\alpha 1,2}$ characteristic radiation, following the ASTM E975-13 standard [9]. Hardness measurements were completed by the Vickers (HV 10) method. Seven measurements were made for the specimens processed at any heat treatment schedules and both the mean values and the standard deviations were then calculated.

3.   RESULTS AND DISCUSSION

Fig. 1 shows optical micrographs of conventionally quenched specimen and SZT specimen with duration of SZT of 17 h. The microstructure manifests uniform distribution of carbides throughout the matrix in both cases. The matrix is composed of the martensite, blue/dark colored and the γ_R (brown-colored) whereas it is clearly shown that the amount of γ_R is much lower in SZT specimen. The maximal size of regularly shaped carbides is roughly around 3 μm but dominant part of particles has a size around 1 μm or less. Also, here is clearly shown that the SZT makes the carbides finer and their number enhanced, compared to conventionally quenched specimen.

SEM micrographs (**Fig. 2**) clearly delineate the differences in amounts of carbides of differently SZT specimens. The material contains eutectic carbides (ECs), secondary carbides (SCs) and small globular carbides (SGCs). The etching technique, coupled with combined detection regime of backscattered and secondary electrons makes clear difference between ECs and other carbides, due to difference in backscattered electron yield. Hence, the ECs appear dark because they contain higher amount of lower atomic vanadium and carbon while others particles (e.g. SCs and SGCs) appear bright since they contain less carbon and more iron and chromium, respectively.
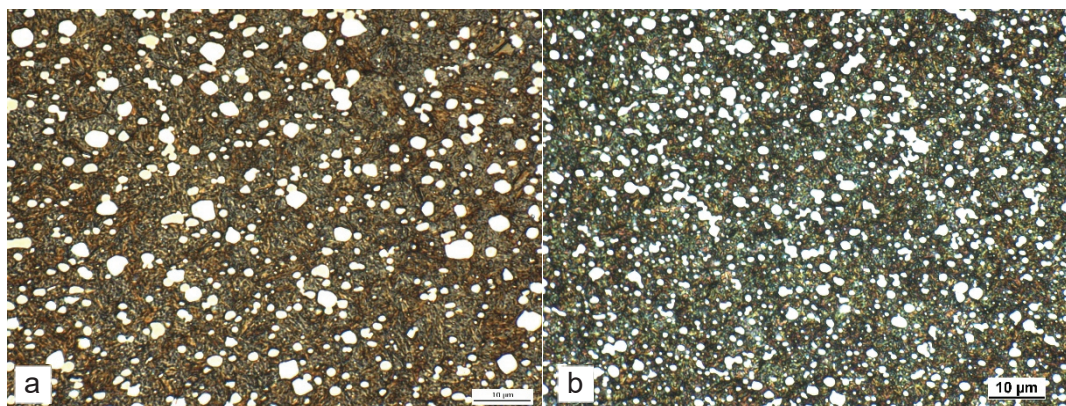
Fig. 1 Light micrographs showing the microstructure of the Vanadis 6 ledeburitic steel: a - after conventional quenching, b - after sub-zero treatment with duration of 17 h
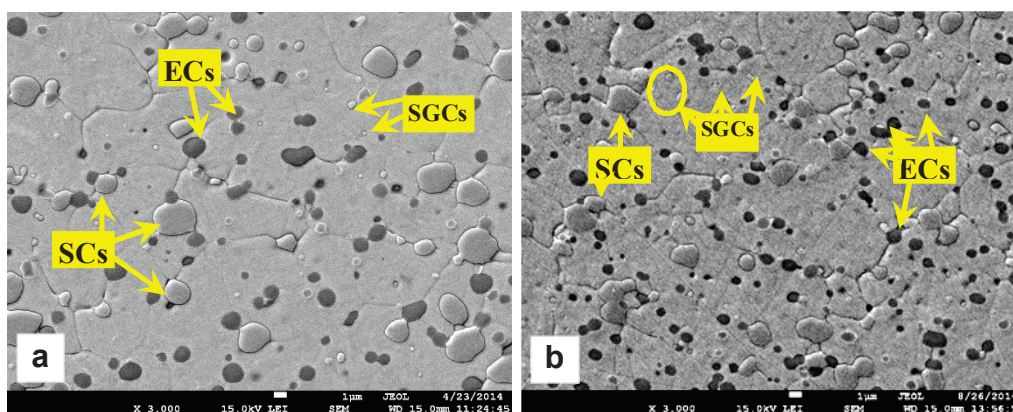

Fig. 2 Representative SEM micrographs showing the microstructure of the Vanadis 6 ledeburitic steel: a - after conventional quenching, b - after sub-zero treatment with duration of 17 h

The amounts of both the eutectic carbides (ECs) and the secondary carbides (SCs) are almost invariable for differently heat treated specimens, **Table 1**. This finding is consistent with logical postulate that the amount, size and distribution of ECs can be modified only using the liquid-phase treatment, by variations of solidification conditions and, that the amount of SCs should be constant when identical austenitizing conditions (temperature and time) are used for treatments.

It is shown in **Table 1** that the application of sub-zero treatment (-196 °C/17 h) led to reduction in the amount of retained austenite to the values close to the detection limit of X-ray diffraction. This is in relatively good agreement with literature data reported recently [3, 12] for sub-zero processed AISI D2 and X220 CrMoV 13-4 steel, respectively, where it is reported that the amount of the γ_R lies around 2% after long-time SZT.

Table 1 Quantitative microstructural parameters of the Vanadis 6 steel after conventional quenching and SZT

Sub-zero treatment [h]	Population density [1000/mm²]			Amount of retained austenite [vol.%]
	ECs	SCs	SGCs	
-	79.9 ± 2.3	30.8 ± 1.5	25.5 ± 1.7	20.2 ± 1.6
17	85.0 ± 3.1	28.8 ± 1.0	72.4 ± 2.4	2.1 ± 0.5

TEM micrographs, **Figs. 3, 4** clearly delineate differences in sub-structure of the material processed by conventional quenching and that of sub-zero treated. The matrix of conventionally quenched specimen consists of relatively coarser martensite and larger islands of γ_R while that of SZT sample clearly exhibits

indications of refinement of martensitic domains and, also significantly reduced amount of retained austenite. The formations of retained austenite are located mainly at the interfaces between the martensitic domains.
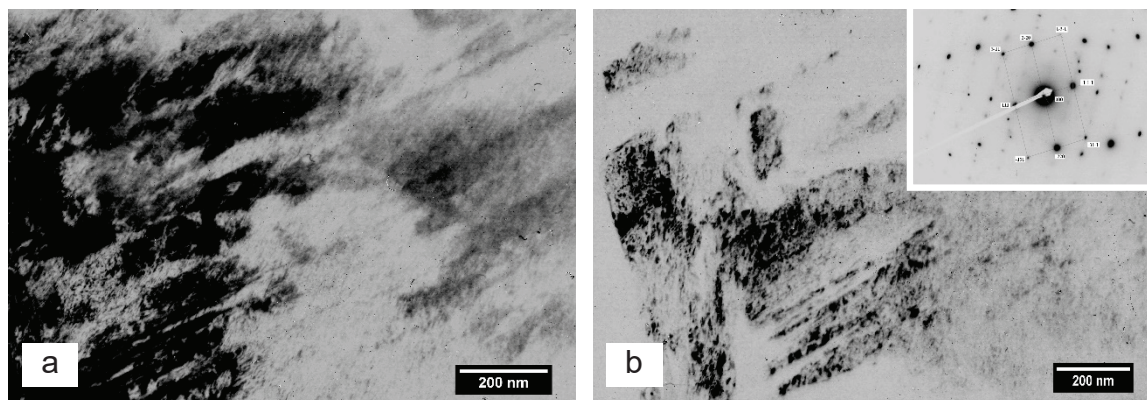

Fig. 3 Microstructure of the material after: a) conventional quenching, bright field image, b) the same place, dark field image with the diffraction patterns of retained austenite
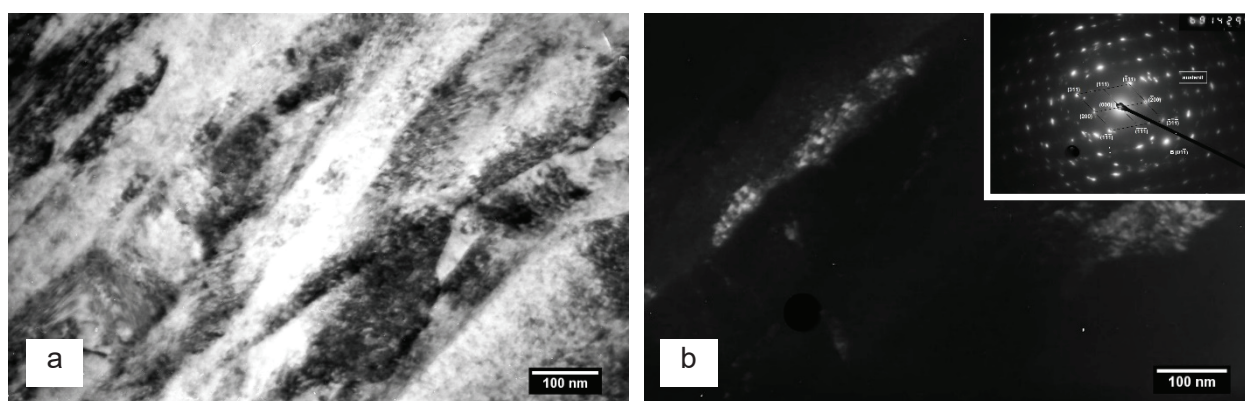

Fig. 4 Microstructure of the material after: a) SZT for 17 h, bright field image, b) the same place, dark field image with the diffraction patterns of retained austenite

Refinement of martensite produced by the SZT has been reported recently [7, 12]. However, the principal explanation of it absents up to now and it was only hypothesised that mentioned refinement of martensite can be referred to the fact that at least a part of martensitic transformation takes a place at constant temperature -196 °C and, exhibits indications of time-dependency. The formation of martensitic domains would be controlled by plastic deformation of supercooled austenite (albeit very slow) and by carbon clustering by moving dislocations, as suggested in [11]. Hence, the size of martensitic domains may be smaller due to strong thermal limitations in the kinetics of isothermal γ to α' transformation. The population density of SGCs was found to be higher for SZT material, which is in line with the most relevant studies made by Das et al. [3, 4]. In these papers it was demonstrated that the amount of these particles increases with decreasing the lowest treatment temperature and also, with prolonging the duration of SZT, up to the maximum at 36 h. The interpretation of obtained experimental data, however, seems to be misleading. The mechanism associated with modification of number and interparticle spacing of SGCs was hypothesised as follows [4]: Cooling of the steel to sub-zero temperature results in more complete γ to α' transformation. This transformation is associated with development of internal stresses that are higher in SZT than what is achieved in classical quenching. Different thermal contraction of austenite and that of martensite also contributes to the development of internal stresses. As a result, higher density of lattice defects is generated in martensite formed during SZT and, the supersaturation of martensite is higher, also. These phenomena increase thermodynamic instability of

martensite, which results in segregation of carbon atoms to nearby crystal defects forming clusters. These clusters can either act as or grow into nuclei for the precipitation of carbides during subsequent tempering treatment. Enhanced amount and population density of small globular carbides is, according this hypothesis, explained by accelerated precipitation due to SZT. Other theory, which was adopted by the group of investigators Amini et al. [5, 10] have claimed that the austenite and the martensite endure high degree of contraction when cooled down from the austenitizing temperature and that the contraction is greater in sub-zero treatment. The carbon atoms cannot be stable at their places in deformed martensitic lattice and they are forced to jump to neighbour dislocation acting as preferential sites for further carbide precipitation during tempering.

However, these theories are at variance with obtained results reported in [11, 12]. It is claimed here that carbon atoms are immobile below a temperature of about -50 °C, hence, the probability of their jumping or segregation to nearby crystal defects is unlikely. The only possibility to form carbon clusters is thus their caption by moving dislocations, as a consequence of plastic deformation of freshly formed martensite during the isothermal hold at the cryotemperature. Another question is whether the SGCs can precipitate at low temperatures or, in particular, during SZT. As found for instance in [1, 11], intermediate precipitates of ε-carbides (or η-carbides) formed at low temperatures (up to 200 °C) are needle-like particles with a length of several tens of nm and much smaller width. On the other hand, the SGCs are much coarser and hence, it is unlikely to be formed by classical precipitation. Hence, the formation of SGCs must be associated with another phenomenon. One can, for instance, suggest the following hypothesis:

i) Martensitic transformation is associated with approx. 4.3% volume expansion, which causes a development of internal stresses in the steel. Formation of internal stresses is further promoted by differences in thermal expansion coefficient of the martensite and that of the austenite. One can expect that these stresses increase with more completed martensitic transformation, e.g. due to SZT. Due to extensive stress situation, the material is forced to relief these stresses.

ii) The Vanadis 6 steel has a specific density of 7610 kg/m^3 when quenched and tempered to secondary hardness of 60 HRC [13]. In this context it should be noticed that the tempered martensite is in much weaker stress situation than that after quenching/SZT and, expectedly, it has higher specific density. One can thus expect that no-tempered martensite would have lower specific density, approx. 7400 - 7500 kg/m^3. Other major phases that are present in the material after sub-zero treatment are the carbides, namely MC and M_7C_3. The specific density of MC-carbide and M_7C_3-carbide was reported to be 5607 - 5640 and 6920 kg/m^3, respectively [14, 15].

iii) Small globular carbides were identified as alloyed orthorhombic cementite [7]. The cementite has similar specific density (e.g. 7.62 g·cm^{-3} [16]) as the martensite.

The consideration implies that during the SZT, the phase with the highest possible specific density (cementite) is formed, which can be associated with the effort of the material to lower the internal stresses. **Fig. 5** shows tempering charts of conventionally quenched samples and SZT ones. The hardness of no tempered material is higher when sub-zero treated, which can be referred to almost complete removal of retained austenite and to the presence of enhanced population density of SGCs. In both types of samples, tempering at low temperatures induces decrease in hardness whereas the hardness of SZT steel is higher than that of conventionally quenched one, by 50 - 100 HV10. As clearly evident, SZT material has lost the secondary maximum peak while conventionally quenched steel manifests this maximum when tempered at a temperature of 530 °C. This can be referred to different phase constitution of the samples before tempering, e.g. the SZT material contains much less retained austenite and much more small globular carbides. The latest is associated with depletion of martensite, thus, lower contribution of carbides precipitation gives, apart from negligible effect of the transformation of the γ_R to the martensite, the principal explanation of the absence of secondary hardening peak in sub-zero treated material.
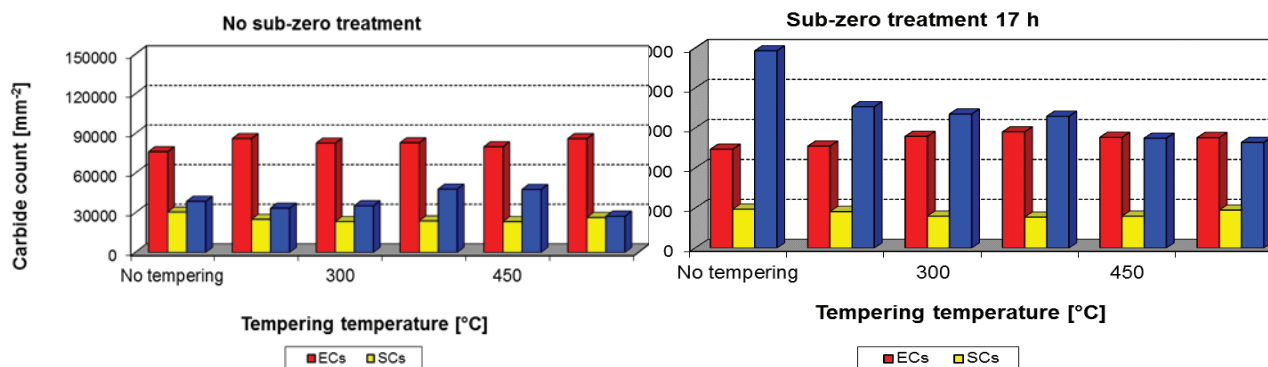
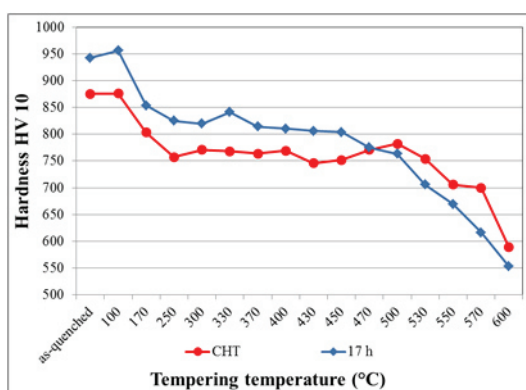**Fig. 5** Tempering charts of conventionally quenched and SZT (17 h) Vanadis 6 steel

Fig. 6 Variations of carbide amounts in differently heat treated Vanadis 6 steel

Fig. 6 shows the variations in amounts of carbides as a result of sub-zero treatment and tempering. There are not significant differences in amounts of ECs and SCs in differently heat treated specimens. On the contrary, there is a considerable increase in the amount of SGCs due to sub-zero treatment. As a result of tempering, the amount of SGCs changes in very limited extent in conventionally quenched specimens while that in SZT samples manifests a clear decreasing tendency with increasing the tempering temperature. The following consideration can be made with this respect: It is known that tempering induces decomposition of martensite, transformation of retained austenite and, as a result, changes in hardness of the steel, **Fig. 5**. Apart from these changes, also the reduction of internal stresses introduced during quenching and SZT takes place. As abovementioned, there is a hypothesis that it is an extensive stress situation being responsible for the formation of SGCs in sub-zero treatment. The finding that the amount of SGCs decreases with increasing the tempering temperature assists to support this hypothesis. In other words, it seems that reduction of internal stresses, due to tempering, induces dissolution of certain amount of SGCs.

4.   CONCUSIONS

The obtained results allow make the following major conclusions:
1) The material consists of matrix, composed of the martensite and retained austenite, and carbides, namely eutectic, secondary and small globular carbides, irrespective to the heat treatment applied.
2) Sub-zero treatment refines the martensite, reduces the amount of retained austenite and increases the population density of small globular carbides.
3) Tempering of sub-zero treatment induces a decrease in hardness and loss of secondary hardening peak. The hardness of SZT material is higher than that of conventionally treated steel but it is lower in high temperature tempering range.

4) The presence of SGCs in sub-zero treated material is not as a result of "acceleration of precipitation rate" but probably originates from enhanced stresses due to the SZT

ACKNOWLEDGEMENTS

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