Microstructural Evaluation of Tool Steel Vanadis 6 after Sub-Zero Treatment at -140 °C without Tempering

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The microstructure, phase constitution and hardness of Cr-V ledeburitic tool steel Vanadis 6 subjected to sub-zero treatment at -140 °C and for different soaking times have been investigated. The microstructures have been characterized using the light microscopy, scanning electron microscopy and X-ray diffraction. The metallurgical aspects include the reduction of the retained austenite amount and increase in carbide count, as compared to conventionally heat treated material. The matrix is martensitic with certain amount of retained austenite, irrespectively to the time of sub-zero treatment. The amount of retained austenite has been significantly decreased from 20.2 vol. % to minimum 3.2 vol. % at 48 h soaking time. The microstructure of sub-zero treated steel contains eutectic, secondary and increased count of small globular carbides. The count of small globular carbides for conventionally heat treated samples was around 48 x 10^3 / mm^2 and for sub-zero treated samples was increased more than four times with maximum 209 x 10^3 / mm^2 at 24 h soaking time. These particles have size of up 500 nm but 100 nm in most cases. The hardness has been increased as compared to no sub-zero treated samples from 875 ± 16 HV 10 up to 954.6 ± 14 HV 10 at holding time 48 h.

Keywords: Sub-zero Treatment, Carbides, Martensite, Microstructure, Ledeburitic Steel

1 Introduction

One of major problems of high carbon steels processed by conventional heat treatment is too high amount of retained austenite after hardening procedure. For example, Jurči et al. [1] have reported that the amount of retained austenite for conventional heat treated samples of Vanadis 6 austentized at 1050 °C was 20.2 ± 1.6 vol. % and it was reduced to 9.9 ± 1.6 vol. % after sub-zero treatment at -196 °C for 4 h. Sub-zero treatment (SZT) is the process of cooling a material to temperatures far below room temperature. The SZT in liquid nitrogen -196 °C leads to changes in structure and properties. Some of claimed benefits of SZT include the increase in wear resistance, better dimensional stability and hardness increase [2, 3, 4]. Literature data on the improvement of the wear resistance of Cr-and Cr–V ledeburitic steels shows a property increase that varies from several tens of percent up to almost 1000% [5].

We more often encounter investigation of SZT in liquid nitrogen at -196 °C. However, some researches indicate that SZT at higher temperatures could have more beneficial effect on changes in the microstructure. The treatment of steels at temperatures in the range −80 °C to −120 °C is usually sufficient to fully transform any austenite retained in the quenched microstructure [3]. If the driving force were increased by cooling to a lower temperature, then it might be possible to form carbides in the martensite formed at low temperatures, thus maximising performance with a combination of high hardness and nano-sized ε-carbide dispersion. The obvious choice of refrigerant would be liquid helium at −269 °C (4 K). However, it is inevitable that treatment times would be very long as there is little atomic movement at such a low temperature [3].

Reitz et al. [5], for instance, demonstrated an increase of hardness when the SZT was done at -140 °C compared to -196 °C. In this article, the results of experimental investigations of differences between conventionally heat treated (CHT) Vanadis 6 steel and the same steel processed by sub-zero treatment at -140 °C, with particular attention to the microstructure, amount of retained austenite and hardness are demonstrated and discussed.

2 Experimental

The experimental material was the tool steel Vanadis 6 with nominally 2.1 % C, 1.0 % Si, 0.4 % Mn, 6.8 % Cr, 1.5 % Mo, 5.4 % V and Fe as balance, made by PM. Samples for the microstructural investigations were cylinders with 17 mm in diameter and height of 6 mm. Conventional heat treatment (CHT) consisted of the following steps: heating up to the austenitizing temperature of 1050 °C in a vacuum furnace, holding at the temperature for 30 min and nitrogen gas quenching (5 bar). SZT has been applied after quenching in liquid nitrogen vapor (-140 °C) for 4, 10, 17, 24, 36 and 48 hours. No tempering of the steel was carried out in order to highlight the microstructural changes due to SZT itself.

Metallographical samples were prepared by standard preparation line and etched with the Villela-Bain reagent for the light microscopy or with a picric acid for the SEM-observation.

The microstructure was recorded using the light microscope NEOPHOT 32 and the scanning electron microscope JEOL JSM 7600 F device equipped with an EDS-detector (Oxford Instruments), at an acceleration voltage of 15 kV. For details of the categorization of the carbides check the Refs [1, 6]. The amount of retained austenite (γR) was measured by X-ray diffraction, according to the ASTM E975-13 standard [7]. X-ray patterns were recorded using a Phillips PW 1710 device with filtered Coα1, 2 characteristic radiation, in the range 20-144° of the two-theta angle. Macro-hardness measurements were completed by the Vickers (HV10) method.

Each metallographic specimen was measured for 5 times, and the mean value and standard deviation from the measurements of each specimen was calculated.

3 Experimental Results, Discussion

Figure 1 shows light micrograph of the examined steel after conventional quenching followed by SZT for 17 h. The microstructure consists of matrix and undissolved carbides. The matrix contains the martensite and retained austenite. The austenite grain size G was determined by Snyder-Graff method by formula

$$G = [\ 6.635\ \log\ (S - G)\ ] + 2.66\ [-], \qquad (1)$$

Where:
(S–G)…Snyder-Graff intercept count number [-].

The grain size was determined to be 10.26 ± 0.14. The count of small globular carbides increases in comparison with convectional heat treated samples, however, optical microscopy fails to bring more details. This was also confirmed in previous research by Das et al. [8] and Surberg et al. [9].

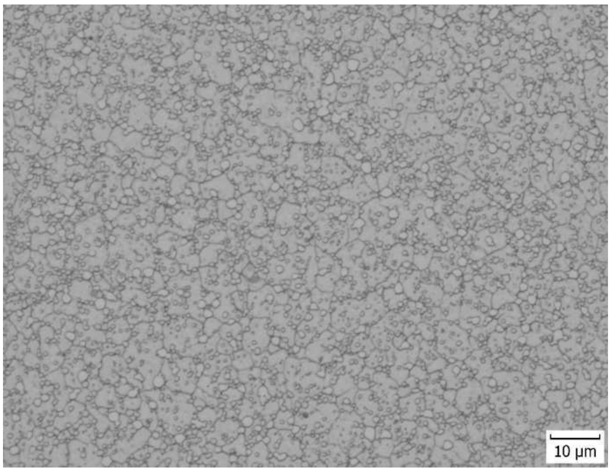

***Fig. 1** Light micrograph showing the microstructure of the Vanadis 6 after SZT at -140 °C for 17 h.*

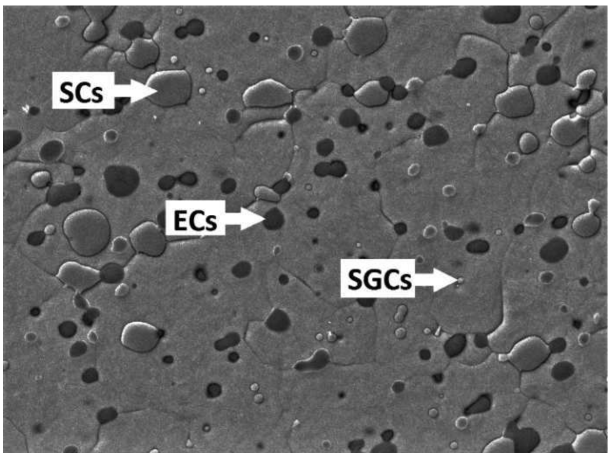

***Fig. 2** Microstructure of Vanadis 6 after CHT*

SEM micrographs, Figures 2, 3 show examples of typical microstructures of the Vanadis 6 tool steel after CHT and after SZT at -140 °C for 4 h. The microstructure is composed of the matrix and three types of carbides: eutectic carbides (ECs), secondary carbides (SCs) and small globular carbides (SGCs). The count of ECs and SCs is invariant over the heat treatment parameters range used in experiments because the ECs do not undergo the dissolution during austenitizing, and the level of dissolution of the SCs is constant at fixed austenitizing temperature. The population density of SGCs increased with holding time at the temperature of SZT. This is clearly evident by comparing of the microstructures in Figure 2 and 3, respectively. Figures 4, 5 show SEM micrographs of samples after SZT at -140 °C for 24 h and 48 h, in these micrographs it is clearly shown that the increase in population density of SGCs is highlighted at long durations of SZT.

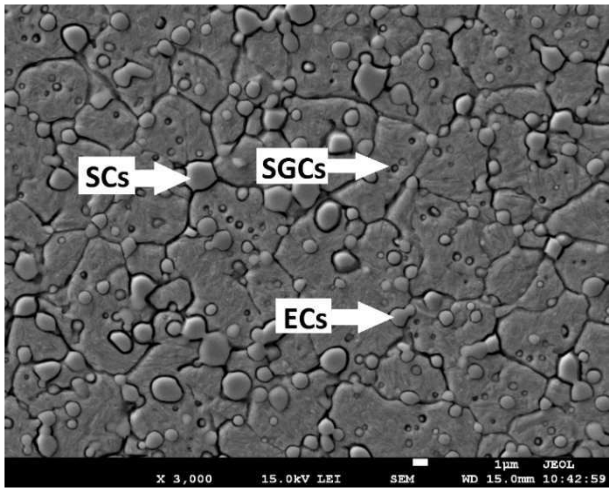

***Fig. 3** Microstructure of Vanadis 6 after SZT at -140 °C for 4 h*

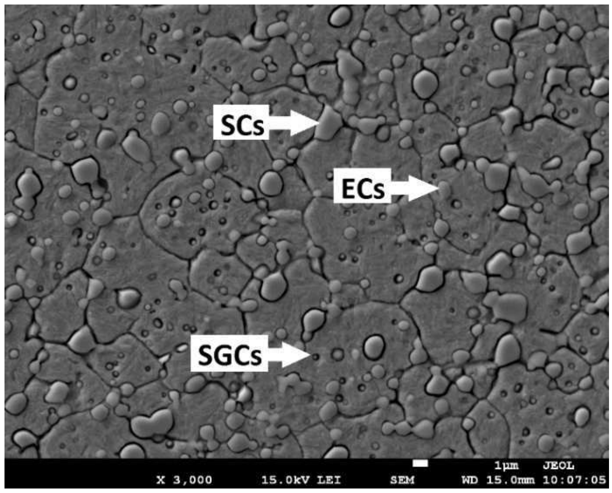

***Fig. 4** Microstructure of Vanadis 6 after SZT at -140 °C for 24 h*

The population density of SGCs as a function of the duration of SZT is shown in Figure 6. It is obvious that the population density of SGCs increased very rapidly up to 24h of soaking time. The mean values of population density of SGCs were 48 x 103, 176 x 103, 179 x 103, 198 x 103, 209 x 103, 193 x 103 and 183 x 103 / mm2 for CHT samples and SZT samples for 4, 10, 17, 24, 36 and

48 h, respectively. Here it should be noted that the values, with respect to the statistical uncertainty at a level of 95 %, considerably overlap for the samples treated for 4 and 10 h. It is shown that the maximum population density of SGCs was achieved for 24 h storage time at -140 °C.

The size of SGCs is about 500 nm but more typically around 100 nm. Enhanced population density of SGCs is in good agreement with previous studies, by Das et al. [10], for instance. On the other hand, the explanation of the formation of SGCs, as suggested in this study is rather confusing. Das et al. [10] suggested that enhanced population density of carbides is due to acceleration of precipitation rate during tempering. However, it is unlikely to expect the precipitation of these carbides, at low temperatures, by thermal activated atom transport. In addition, the particles of SGCs were observed already after SZT and reheating to room temperature in the present study. Hence, one can suggest that the reason for the presence of SGCs can differ from what was proposed by Das et al. [10], as discussed later in the paper.

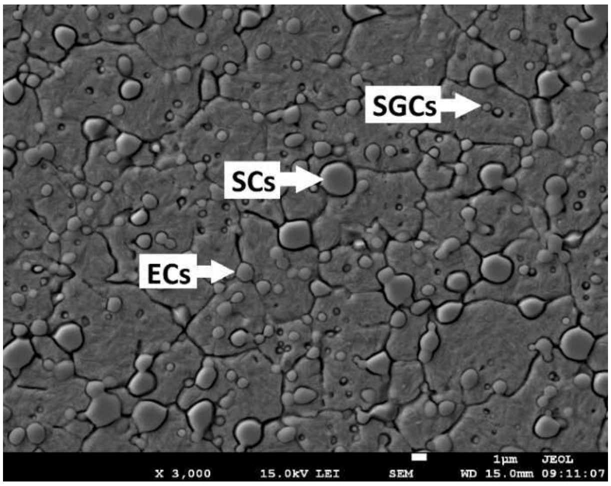

Fig. 5 *Microstructure of Vanadis 6 after SZT at -140 °C for 48 h*

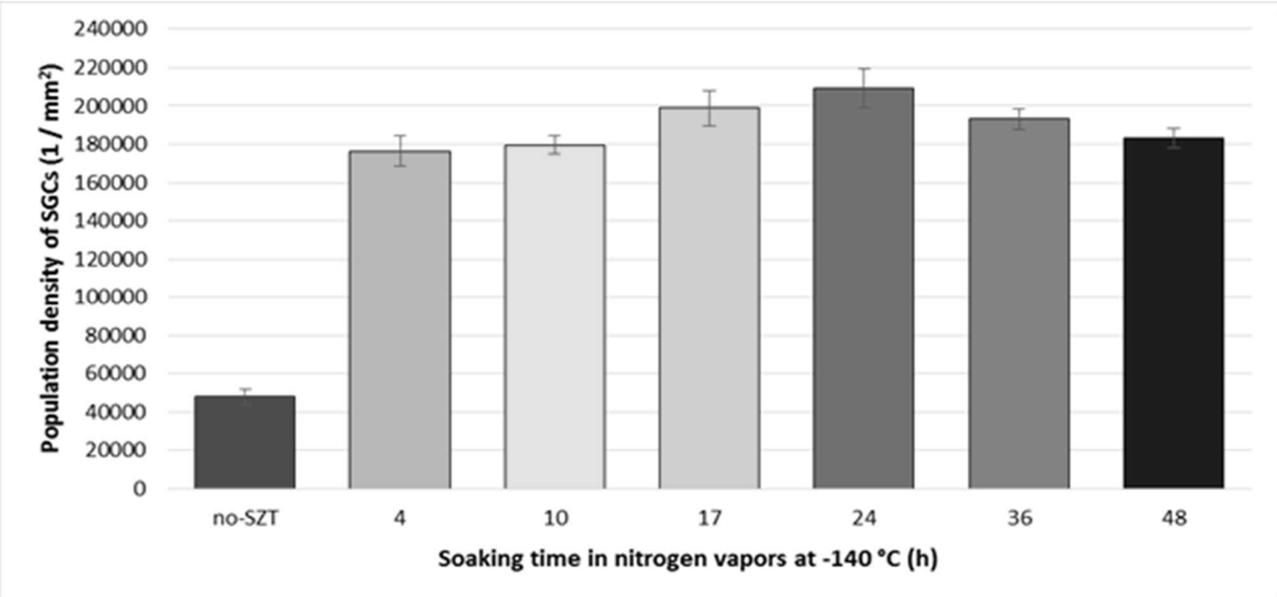

Fig. 6 *Population density of SGCs for samples processed by CHT and SZT, with various soaking times in nitrogen vapors.*

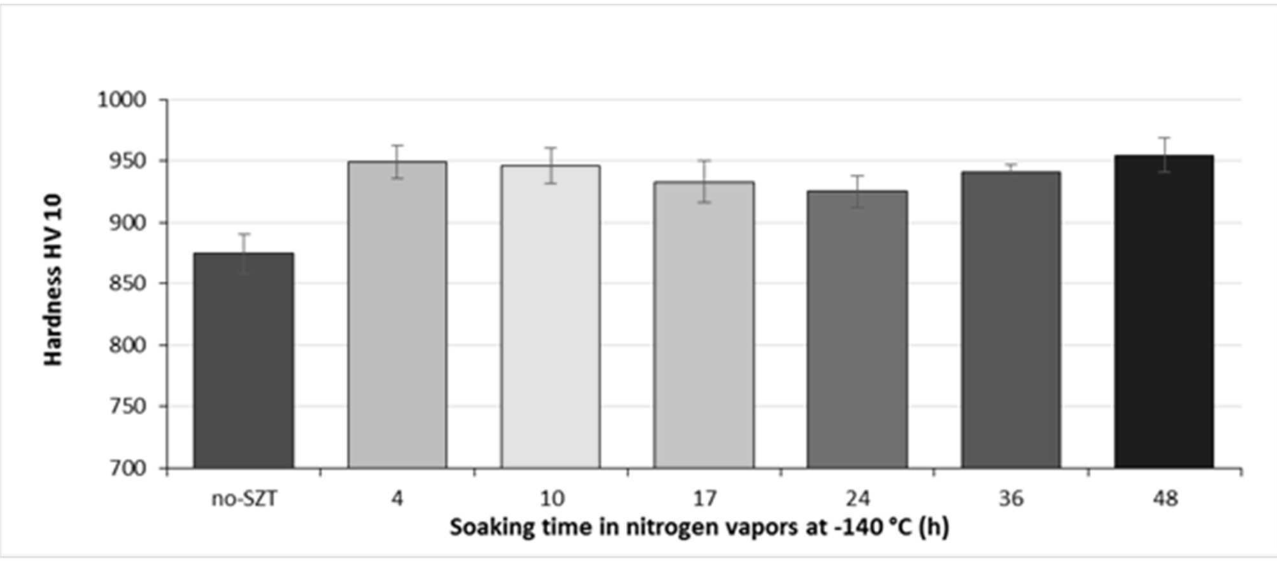

Fig. 7 *Bulk hardness HV 10 of the Vanadis 6 after SZT with different soaking time in nitrogen vapors.*

The bulk hardness of SZT Vanadis 6 tool steel is shown in Figure 7. The hardness of CHT steel was 875 ± 16 HV 10. The hardness of the SZT steel soaked in nitrogen vapor for 4, 10, 17, 24, 36 and 48 h were 949 ± 13.5, 949.2 ± 15.6, 933.2 ± 16.8, 925.2 ± 13.3, 940.8 ± 6.4 and 954.6 ± 14 HV 10, respectively. These results infer that the as-quenched bulk hardness of Vanadis 6 steel is improved due to SZT, whereas the improvement is almost independent on soaking time in nitrogen vapors. In other words, the application of SZT at -140 °C increases hardness compared to the state after CHT, but the effect of SZT can be considered as minimal for durations of this treatment longer than 4 h.

The γ_R amount decreases considerably with the application SZT, Table 1. In no-SZT samples the amount of γ_R was 20.2 vol. % and for SZT samples with 48 h holding time it was just 3.24 vol. %.

Tab. 1 *Amount of retained austenite (vol. %) in the SZT samples for various soaking time (h)*

SZT (h)	No-SZT	4	10	17	24	36	48
γ_R-amount (vol. %)	20.2	3.94	4.64	4.25	4.16	3.6	3.24

The obtained results are consistent with results in other publications [10, 12]. These researchers have reported that the AISI D2 steel is almost free of γ_R after SZT performed at -196 °C for 36 h. Tyshchenko et al. [13] have established that Cr-V ledeburitic steel X220 CrMoV 13-4 contained around 4 % of retained austenite after long-term SZT at -196 °C. It is relevant to note that the γ_R always exist in their microstructure after quenching and before tempering and the martensitic transformation is never completed in high-carbon ledeburitic steels.

As reported by Villa et al. [15], the retained austenite of 100Cr6 ball bearing steel manifested high compressive stresses after application of SZT. Table 2 shows calculated hydrostatic stresses for differently SZT samples. The stress values have been calculated from the lattice deformation (true strain), assuming pure elastic deformation (validity of Hook´s law), and considering the Young modulus to be 225 GPa [14]. It is shown that the compressive stresses in the retained austenite exceed 1000 MPa, and that the highest stresses were developed in the material that was SZT for 24 h. Fig. 8 shows the dependence of carbide count (1 / mm^2) and compressive stress (MPa) on the duration of SZT. Correlation coefficient for dependence of carbide count and stress was calculated to be 0.858961. The correlation coefficient is greater than 0.8, hence, there is a strong linear dependency of these parameters.

Tab. 2 *Compressive stress σ (MPa) in the SZT samples for various soaking time (h)*

SZT (h)	**Lattice deformation ε (-)**	**Compressive stress σ (MPa)**
4	0.005539	1246
10	0.006517	1466
17	0.006746	1518
24	0.007199	1620
36	0.006786	1527
48	0.006411	1442

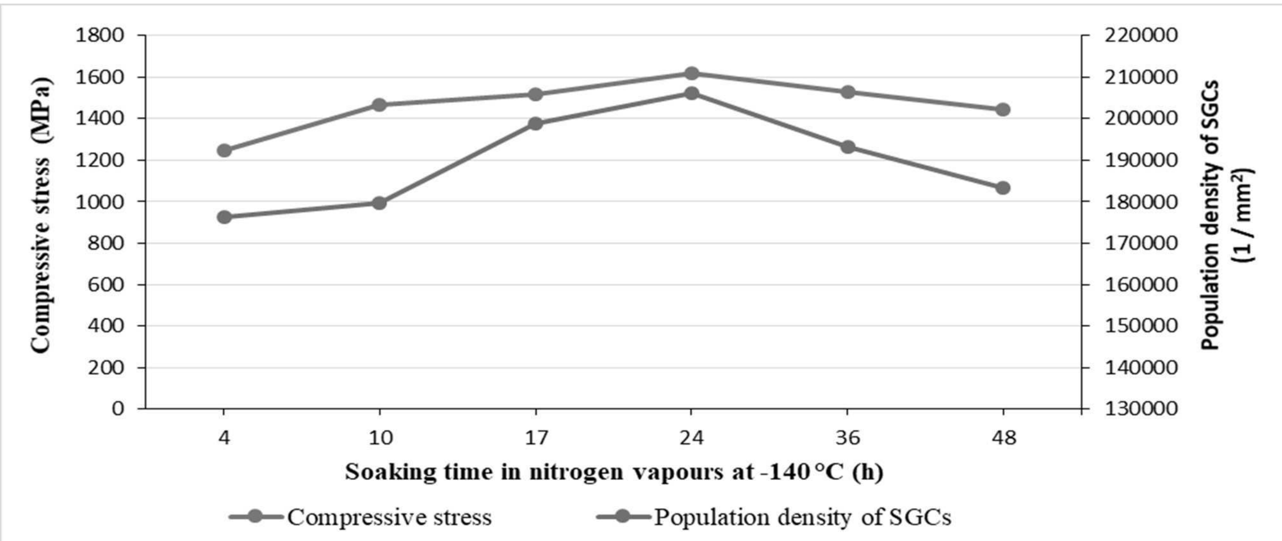

Fig. 8 *Dependence of population density of SGCs and compressive stress at various soaking time.*

In order to explain the presence of considerably enhanced population density, the following consideration can be used: As well known, the martensitic transformation is never completed in high-carbon steels. This is due to very low martensite finish (M_f) temperature (it lies well below the room temperature in most cases), and also due to the positive volumetric effect of the transformation. As a result, compressive stresses are built up in the austenite, which hinder further progress in the transformation. In SZT, however, the temperature lies well below the M_f, and this makes a strong driving force for continuing of the transformation. As discussed and explained recently [11], the SGCs are a by product of the martensitic transformation that takes place at cryotemperatures, and resulted from the effort of the material to relax the stresses and thereby enabling the further martensitic transformation. In the present study, close correlation between the compressive stress in the retained austenite and the population density of SGCs has been established. This is an additional supporting fact to the theory, which was elaborated and demonstrated recently [11].

4 Conclusions

The obtained experimental results lead to following major conclusions:

- The SZT Vanadis 6 tool steel is composed of the matrix (the martensite and the retained austenite), ECs, SCs and SGCs (with a size up to 500 nm, mostly around 100 nm).
- The count of small globular carbides is several times enhanced due to the SZT, with a maximum after SZT realized for soaking time of 24h.
- The application of SZT reduces the amount of retained austenite in Vanadis 6 tool steel.
- The as-quenched hardness of the Vanadis 6 tool steel manifests a marginal increase after SZT.
- There is a strong linear dependency of population density of SGCs and compressive stress. Correlation coefficient for dependence of these parameters was calculated to be 0.858961.

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