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Investigation of Microstructure of Differently Sub-Zero Treated Vanadis 6 Steel

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***Abstract*—**Ledeburitic tool steel Vanadis 6 has been subjected to sub-zero treatment (SZT) at -140 °C and -196 °C, for different durations up to 48 h. The microstructure and hardness have been examined with reference to the same material after room temperature quenching, by using the light microscopy, scanning electron microscopy, X-ray diffraction, and Vickers hardness testing method. The microstructure of the material consists of the martensitic matrix with certain amount of retained austenite, and of several types of carbides – eutectic carbides, secondary carbides, and small globular carbides. SZT reduces the retained austenite amount – this is more effective at -196 °C than at -140 °C. Alternatively, the amount of small globular carbides increases more rapidly after SZT at -140 °C than after the treatment at -140 °C. The hardness of sub-zero treated material is higher than that of conventionally treated steel when tempered at low temperature. Compressive hydrostatic stresses are developed in the retained austenite due to the application of SZT, as a result of more complete martensitic transformation. This is also why the population density of small globular carbides is substantially increased due to the SZT. In contrast, the hardness of sub-zero treated samples decreases more rapidly compared to that of conventionally treated steel, and in addition, sub-zero treated material induces a loss the secondary hardening peak.

***Keywords*—**Microstructure, Vanadis 6 tool steel, sub-zero treatment, carbides.

I. Introduction

INCREASING demand for higher productivity and lowering of manufacturing costs lead to the efforts to improve the performance and durability of tools. These efforts are directed toward the development of new tool steels in one hand and the improvement of existing processing routes in order to fully exploit the potential from the existing tool materials on the other hand. Recent investigations focused on the use of SZT for the enhancement of performance of engineering components, and tools discovered a wide potential of this processing route in this respect.

SZT is an add-on step in the heat treatment of steels, whose austenite is not transformed into the martensite in sufficiently high extent. Ledeburitic Cr and Cr-V steels, high-speed steels and ball bearing steels are typical examples of these materials. Properly applied SZT combined with appropriate tempering regime can substantially reduce the retained austenite amount, make an overall microstructural refinement, and increase the carbide amount [1]. These microstructural changes lead to important variations in industrially important properties such a hardness increase [2], [3], better dimensional stability [4], [5], enhancement in wear performance [6]-[9], and slight improvement of toughness and fracture toughness in selected cases [9], [10].

In SZT, the steels are immersed immediately after quenching into suitable cryo-processing media, held there for pre-determined time, and re-heated to a room temperature. However, the use of various schedules of the SZT developed over the past seven decades rapidly, and the "optimal" temperature of this kind of treatment is not defined yet.

In the 50s and 60s of the 20th century, it was commonly believed that temperatures down to approx. -79 °C (-120 °F) are sufficient to convert high portion of retained austenite into the martensite, and lower temperatures have no practical effect in treatment of steels. Also, the acceptance of these temperatures is a residue of failed trials of heat treaters with direct soaking the tools into buckets or tubs of liquid nitrogen. The resulting thermal shocks led to failure of tools and the companies dropped this idea. However, other treaters tried better controlled treatments, at higher temperatures (mentioned -79 °C, for instance), and obtained promising results. Only much later, a temperature of -196 °C was suggested for treatment. The treatment at the boiling temperature of liquid nitrogen further increased the properties of tools and components. For instance, laboratory test of the wear resistance of SZT AISI D2 steel showed an improvement by 316 % and 817 % when processed at -79 °C and -196 °C, respectively, despite the fact that the hardness manifested only marginal increase [11], [12]. Real industrial trial with either stamping dies or powder compaction dies, made of the same steel, and used for manufacturing a steel furniture showed an increase of durability in the range of hundreds per cents [13], [14].

Only few studies suggested other temperatures, for instance -140 °C [15] or, on the contrary, a temperature of liquid helium [11] for the treatment of Cr-ledeburitic tool steels. The reason is that almost all the experimental works were done by using of liquid nitrogen as a cryoprocessing medium, and the effects of SZTs in liquid nitrogen on the durability of tools are relatively well known. Also, the conservatism of majority metallurgists and scientists plays an important role in common acceptance of a boiling temperature of liquid nitrogen in SZT, and this is why the effect of the use of a temperature of -140 °C has not been investigated yet, and only one study was been focused to the use of liquid He for this kind of treatment [16].

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And finally, it is worth noticing that SZT has changed into a regular science only over the past two decades, which is closely connected with the development of experimental techniques enabling to detect microstructural changes in SZT and conventionally treated samples.

The motivation of the current paper is then to provide the characterization of microstructure of PM ledeburitic steel Vanadis 6, which was subjected to the SZT at -140 °C, and to make a comparison with microstructural characteristics that have been obtained by the SZT in liquid nitrogen. Also, the obtained results are compared to the same material after conventional quenching.

II. Experimental

Commercially available PM ledeburitic steel Vanadis 6 (2.1% C, 1.0 % Si, 0.4% Mn, 6.8% Cr, 1.5% Mo, 5.4% V and Fe as balance) has been used as an experimental material. Specimens were heat treated using following schedules: heating to the austenitizing temperature 1050 °C in a vacuum furnace, hold at the final temperature for 30 min., and nitrogen gas quenching (5 bar). In SZT, conventionally heat treated specimens were cooled down immediately after quenching from the room temperature to the temperature of either -140 °C or -196 °C, stored there for pre-determined time, and then slowly re-heated to the room temperature. No tempering has been done after SZT in order to keep the material state, which was obtained by cooling down to the lowest temperature of the heat treatment cycle unaffected. Metallographic samples were prepared by standard preparation line and etched with a picric acid. The microstructure was recorded using the scanning electron microscopy. For the scanning electron microscopy (SEM), a JEOL JSM 7600F apparatus, equipped with an EDS-detector Oxford Instruments, has been employed, whereas the microstructure was recorded using the secondary electron (SE) detection regime. Hardness of the material in the as-received as well as heat processed conditions was measured by the Vickers method on hardness tester Zwick 3212 (HV 10). Each specimen was measured five times. The mean value and standard deviation from the measurements of each specimen was calculated. For quantification of carbides, 20 randomly acquired SEM micrographs have been used. The methodology of the carbide particles quantification is reported in [9], [10], for instance.

The content of the retained austenite was determined by X-ray diffraction (XRD). X-ray patterns were recorded using a Phillips PW 1710 device with filtered $Co_{K\alpha 1,2}$ characteristic radiation in the range of 45°–127° of the two-theta angle. The amount of retained austenite was evaluated according to the appropriate ASTM standard [17].

III. Results and Discussion

A. Microstructure

SEM micrograph, Fig. 1, shows an example of typical microstructure of the Vanadis 6 tool steel after conventional heat treatment (CHT). The microstructure is formed by martensitic matrix with retained austenite and three types of carbides: eutectic carbides (ECs), secondary carbides (SCs) and small globular carbides (SGCs).

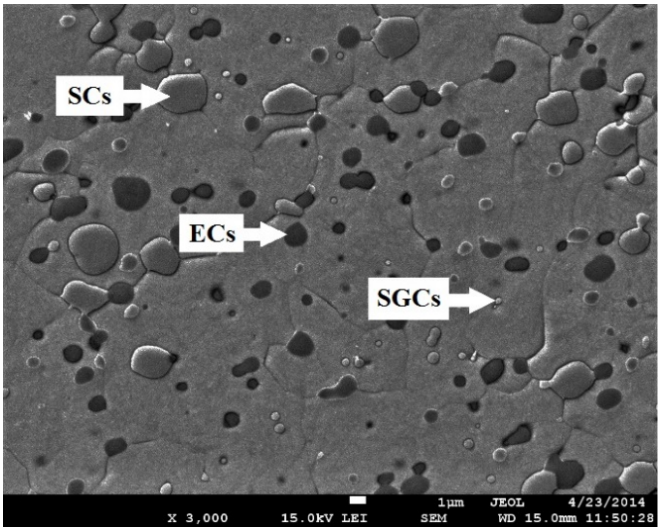


Fig. 1 SEM micrograph showing the microstructure of conventionally heat treated Vanadis 6 ledeburitic steel

SEM micrographs, in Fig. 2, show the microstructure evolution of the material subjected to the SZT at -140 °C compared to what was developed by SZT at -196 °C. The microstructure after SZT consists of matrix composed of martensite and small amount of retained austenite, and of various types of carbides. The population density 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 (note that they are stable practically up to the solidus temperature of the alloy), and the level of dissolution of the SCs is constant at fixed austenitizing temperature. The population density of SGCs increased with the application of SZT. This is clearly evident by comparing of the microstructures in Fig. 1 and Fig. 2, respectively.

B. Quantitative Analysis of Carbides

Recent investigations have shown that the population density of both the ECs and SCs are independent on the SZT [2], [18]. On the other hand, the population density of small globular carbides increased with the application of SZT, with the maximum at a duration of 24 h, Fig. 3. Moreover, it is clearly seen that SZT at -140 °C produces higher population density than that at -196 °C.

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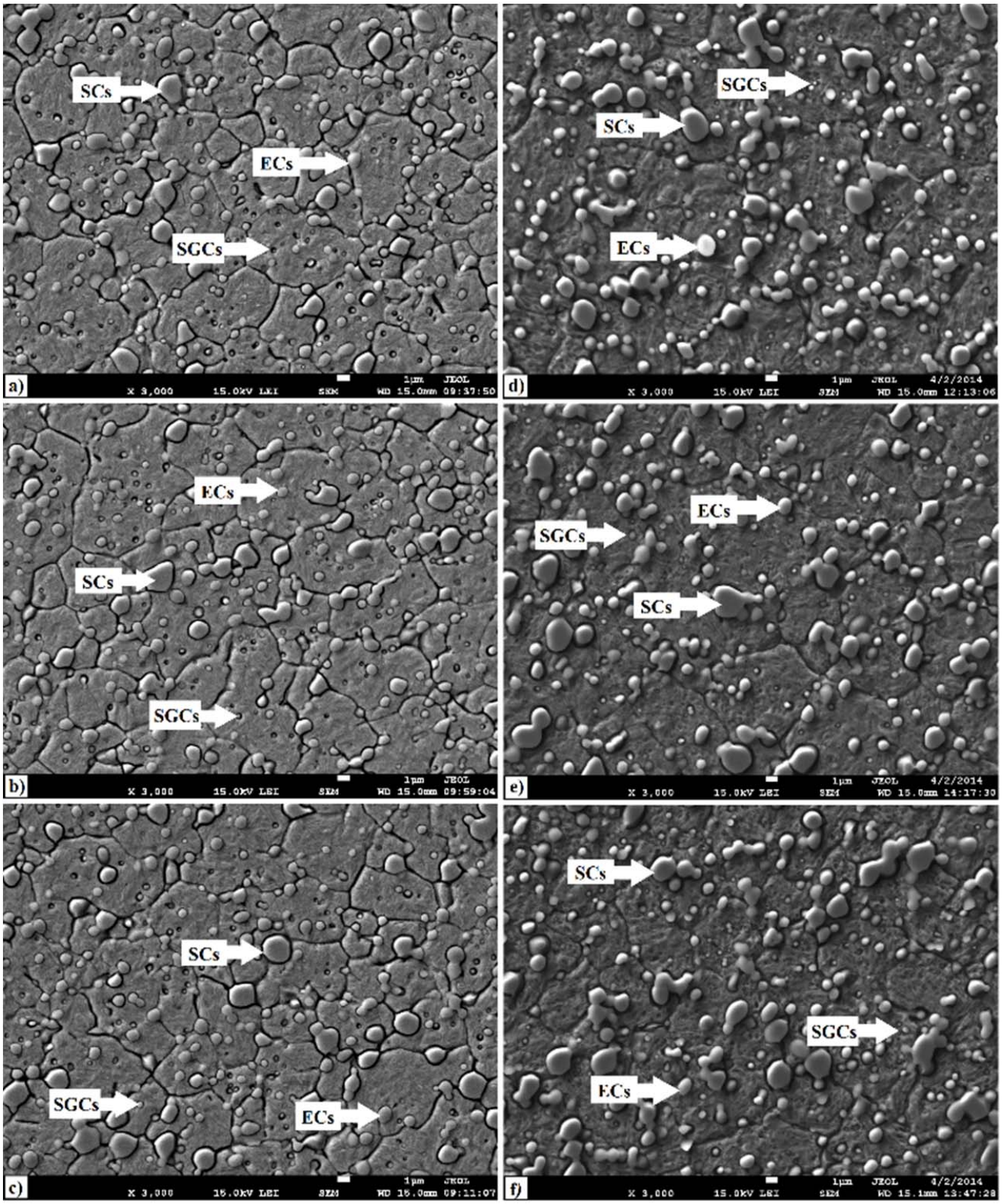


Fig. 2 SEM micrographs showing microstructure of Vanadis 6 ledeburitic steel (a) SZT -140 °C/10 h, (b) SZT -140 °C/24 h, (c) SZT -140 °C/48 h, (d) SZT -196 °C/10 h, (e) SZT -196 °C/24 h, (f) SZT -196 °C/48 h

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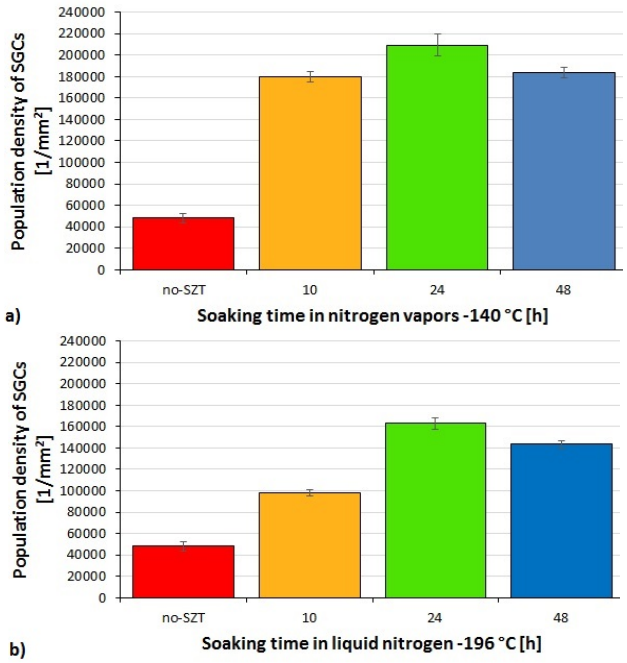


Fig. 3 Population density of SGCs in Vanadis 6 ledeburitic steel (a) SZT -140 °C (b) SZT -196 °C

TABLE I
AMOUNT OF RETAINED AUSTENITE IN VANADIS 6 STEEL AFTER SZT AT -140 °C AND -196 °C

SZT [h]		no SZT	10	24	48
Amount of γ_R [vol. %]	-140 °C	20.2	4.64	4.16	3.24
	-196 °C		2.9	2.9	3.0

Table I shows the amounts of retained austenite in CHT sample and in differently sub-zero treated ones. It is clearly shown that the application of SZT tends to considerable reduction of the retained austenite. In addition, it is shown that the temperature of -196 °C removes the retained austenite more effectively than -140 °C. Also, a time-dependency of the martensitic transformation is evident here for the temperature of -140 °C, while a similar effect has been established for the treatment in liquid nitrogen (-196 °C) at shorter treatment durations [19].

The obtained results are in excellent agreement with recent investigations by Das et al. [3], [20], who found increased population density of carbides in AISI D2 steel after SZT and low-temperature tempering. However, the interpretation of the obtained results differs clearly from that by Das et al. (one can say that the interpretation by Das et al. is misleading and is overcame by existing findings), and is based on the facts that: i) both the austenite and the martensite endure considerable contraction during the cooling down to the lowest temperature of the heat treatment cycle whereas the contraction of the austenite differs from that of the martensite, due to clear difference in the thermal expansion coefficients of these phases, ii) the martensitic transformation is connected with positive volumetric effect, iii) mentioned two phenomena induce a built up of compressive stresses in the retained austenite, and correspondingly tensile strain in the martensite, see [21] for instance.

As a logical consequence, the martensitic transformation would be stopped despite there is high driving force for its further continuation, i.e. the treatment temperature that is well below the characteristic martensite finish point. There is only possibility how the γ to α′ transformation can be more completed, and this is a strain-induced formation of a phase with lower specific volume. Recently, it has been found that the SGCs are of the M_3C nature [2], the population density of SGCs follows the reduction of retained austenite, and also that the tempering treatment tends towards decrease in population density of SGCs [10]. Here, it is demonstrated, in Fig. 4, that there is a very close correlation between the population density of SGCs and hydrostatic compressive stresses in the retained austenite. In the other words, the population density of SGCs increases rapidly at increased compressive hydrostatic stresses in the retained austenite, and both phenomena correspond well to the progress of the martensitic transformation being expressed by the reduction of the retained austenite as shown in Table I. Based on these findings and considerations, one can claim that the formation of SGCs is a by product of more completed γ to α′ transformation rather than a result of acceleration of precipitation.

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 [19]. 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. 4 shows the dependences of the population density of SGCs ($1/mm^2$) and the compressive stress (MPa) on the duration of SZT. The correlation coefficient for these two dependences was established to be 0.858961, which indicates on strong dependency of these parameters.

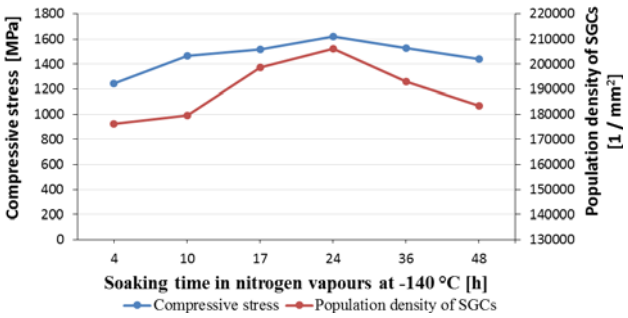


Fig. 4 Dependence of population density of SGCs and compressive stress at various soaking time

Another task is why the SZT at -140 °C produces more SGCs than that in liquid nitrogen. This seems to be a controversial issue since one can assume, according to the obtained results by Villa et al. [21] that the stress state in both the retained austenite and the martensite would be higher after SZT at -196 °C than at -140 °C, and the population density of SGCs would be correspondingly higher when SZT at the temperature of boiling nitrogen. However, one can also logically expect that the plastic deformation of freshly formed

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martensite might be faster at -140 °C, which would logically tend to higher compressive stresses in the retained austenite, producing higher amount of SGCs. Nevertheless, this task seems to be very complex and needs further and extensive study.

C. Hardness

The bulk hardness of no tempered Vanadis 6 steel, as a function of soaking time in liquid nitrogen, is shown in Fig. 5. The as-quenched hardness for conventionally heat treatment steel was 875.0 HV 10 ± 8 HV 10. The hardness of the SZT steel was correspondingly higher, and it exceeds a value of 900 HV 10 significantly. However, the hardness of differently sub-zero treated samples was determined to be almost the same since the statistical uncertainties of the obtained values considerably overlap. These results show that the as-quenched bulk hardness of the Vanadis 6 steel is improved due to the SZT. Similar hardness results achieved by SZT were reported earlier for AISI D2 steel [4], [8], [22]-[26] as well as for AISI D3 steel [6]. The enhancement of as-quenched bulk hardness of SZT steel over the conventional heat treatment can be referred to the reduction of soft retained austenite, corresponding increase in the amount of hard martensite, and to the increased population density of small globular carbides in SZT steel.

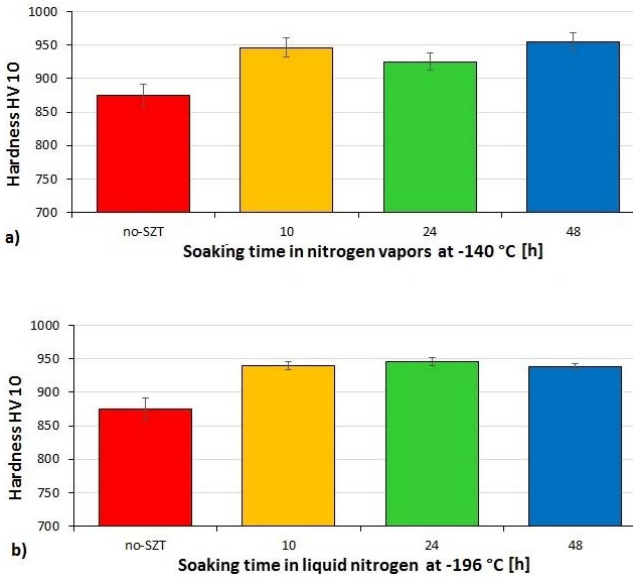


Fig. 5 Hardness HV 10 of Vanadis 6 steel (a) SZT -140 °C (b) SZT -196 °C sub-zero treated for 24

IV. Conclusion

The major findings of the investigations can be summarized as follows:

1) Sub-zero treated Vanadis 6 steel contains martensitic matrix with small portion of retained austenite, the eutectic, secondary, and small globular carbides with a size mostly around 100 nm.
2) SZT reduces the retained austenite amount but this is more effective at -196 °C than at -140 °C.
3) The population density of small globular carbides increases with application of SZT.
4) The as-quenched hardness of the Vanadis 6 steel manifests a moderate increase due to the SZT, and this increase is almost temperature- and time independent
5) The mechanism of formation of SGCs can be hypothesized to be due to extensive stresses in the material due to SZT. This is more probable than the earlier considerations that it is an accelerated decomposition rate of martensite being responsible for formation of SGCs.

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