THE EFFECT OF CONVENTIONAL HEAT TREATMENT AND SUB-ZERO TREATMENT IN LIQUID NITROGEN ON CORROSION RESISTANCE OF VANADIS 6 STEEL

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Abstract

The paper presents the results of the study how the sub-zero treatment of Vanadis 6 steel influences the corrosion resistance of the material. The sub-zero treatment was performed at -196 °C in liquid nitrogen for 17 h. The results obtained by sub-zero treatment were compared with those achieved by conventional heat treatment. The main object of the analysis was the effect of these treatments on the corrosion resistance of the steel tested. Corrosion resistance tests revealed slight improvement in corrosion resistance by the application of sub-zero treatment. Tempering treatment, on the other hand, induced a worsening of corrosion behaviour of the material.

Keywords: Sub-zero treatment, liquid nitrogen, Vanadis 6 steel, corrosion resistance

1. INTRODUCTION

Many heavily loaded components like tools, bearings or gear parts have to be hardened and tempered before use. After hardening it is possible to convert the retained austenite in the martensite by multiple tempering. The tempering at a suitably high temperature produces a fully stable structure of steels, hence, the components may be machined to its final shape and will not distort during use. However, in some cases the tools or components must be tempered at low temperatures, which are insufficient to transform the retained austenite. Sub-zero treatments (SZTs) are the treatments where components are cooled down below the room temperature, held at low temperature, and re-heated to the room temperature. The main purpose of SZTs is to reduce the retained austenite amount, to increase the wear resistance of tools, and to stabilise the products. The temperature of SZT can be very different, from -20 °C to -196 °C. Reactions at low temperatures are slowed down, hence, the duration of SZT has also great importance in the final result of the treatment. Based on many studies it has been established that the optimum SZT needs a minimum of 6h, preferably 12 and more hours [1,2,3,4]. The SZT should be carried out as quickly as possible after quenching because too long delay can reduce beneficial effect of the treatment. A variety of mechanical properties can be improved through SZT. Also the distortions due to quenching can be somewhat better controlled with a sub-zero treatment made immediately after quenching [1,2,3,4].

Tool steels contain primarily martensite and metal alloy carbides which play an important role in good balance between wear and corrosion resistance together with dimensional stability.

Corrosion contributes to gradual destruction of all the materials due to chemical reactions with their environment, and may cause factory shutdowns as a result damage of products, reduction in efficiency, expensive costly maintenance. However, the effect of SZTs on the corrosion resistance of high alloyed tool steels has not been satisfactorily investigated yet. In one scientific paper [5] the authors showed that the corrosion behaviour of deep cryogenically treated AISI D3 Cr ledeburitic tool steel had been enhanced, due to more uniform carbide distribution in association with higher carbide percentage. Alternatively, the same authors claimed that change of parameters of SZT may lead to opposite results [6]. Also, Uygur et al.

demonstrated that the heat treatment that involves the cryogenic period deteriorates the corrosion resistance of AISI D2 steel [7]. It should be noted that corrosion is a phenomenon that cannot be completely eliminated, but it can be significantly reduced.

The current conference paper is a part of comprehensive research, which is devoted to investigations of effect of different SZTs on microstructure, mechanical properties, wear performance and corrosion behaviour of Cr-V ledeburitic tool steels. The aim of this particular work is to analyze the impact of the type of treatment (CHT and SZT) as well as tempering temperatures on changes in corrosion behaviour of Cr-V ledeburitic steel Vanadis 6.

2. METHODOLOGY OF RESEARCH

Chemical composition of Vanadis 6 (Uddeholm AB, Hagfors, Sweden) is presented in **Table 1**. The steel produced by using powder metallurgy is free of macro-segregations and characterized by a high degree of isotropy, which is undoubtedly more beneficial than in conventional steel production.

Table 1 Chemical composition of Vanadis 6 steel [wt %]

C	Si	Mn	Cr	Mo	V	Fe
2.1	1.0	0.4	6.8	1.5	5.4	balance

Plate-like specimens were subjected to the conventional heat treatment (CHT), which consisted of gradual heating up to the austenitizing temperature of 1050 °C in a vacuum furnace (1), holding at that temperature for 30 min (2), and quenching by nitrogen gas. One half of the total number of specimens was, immediately after quenching, subjected to the tempering. The second half of specimens was moved into cryogenic system, where they were cooled down at a cooling rate of 1 °C/min, to a temperature of liquid nitrogen (4). The duration of SZT was 17 h (5). Then, the specimens were re-heated to the room temperature, by a heating rate of 1 °C/min (6). Double tempering (2 h + 2 h) was performed at temperatures 170 °C, 330 °C, 450 °C or 530 °C (7, 8). Schematic of Vanadis steel heat treatment is presented in **Figure 1**.

Microstructural observations were performed on scanning electron microscope JEOL JSM 7600 F coupled with energy - dispersive spectroscope (EDS) Oxford Instruments.

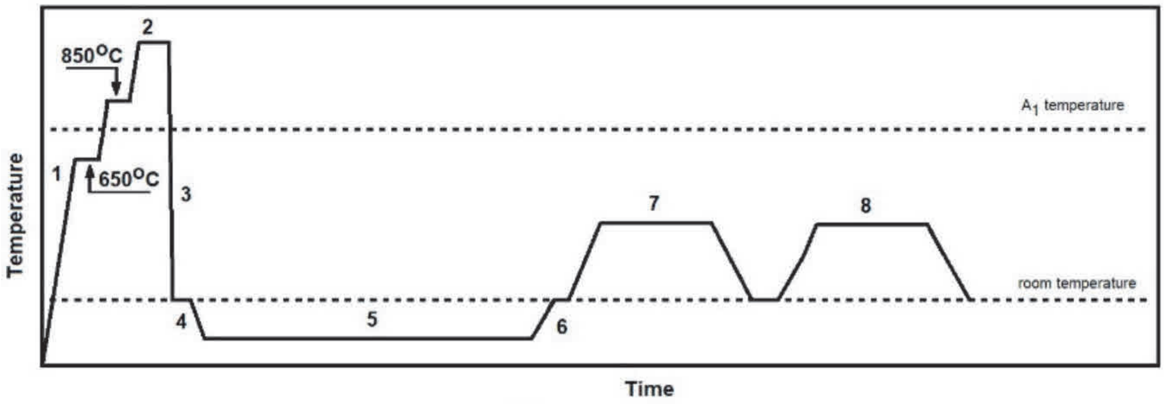

Figure 1 Schematic of Vanadis steel heat treatment

Corrosion resistance was examined via potentiodynamic polarization measurements by using a potentiostat-galvanostat ATLAS 0531 EU & IA ATLAS SOLLICH. The samples were studied in a 3.5 percent concentration NaCl solution, at temperature of 22°C. In the research the auxiliary electrode was a platinum electrode, and the reference electrode was a calomel electrode. The polarization of the samples was carried out in the direction of the anode in the range of potentials from -1.5 V to 1.5 V, and at a rate of potential change of 1 mV/sec.

Based on the analysis of potentiodynamic corrosion curves the corrosion current and corrosion potential were determined. The corrosion rate was calculated according to the ASTM G 102-89(2015)e1 standard.

3. RESULTS

After CHT the microstructure consists of matrix formed by martensite, retained austenite, and three carbide types, namely eutectic carbides (ECs), secondary carbides (SCs), and small globular carbides (SGCs) as reported recently, for instance [1,3], **Figure 2**. It has been found that the character of the matrix microstructure undergoes clearly evident alterations with increasing tempering temperature. As the temperature of tempering increases, precipitation of carbides occurs [3]. It was also noticed that the retained austenite is almost completely removed from the microstructure when tempered at 530 °C. SZT reduces the retained austenite amount and increases the population density of SGCs, **Figure 3**, while the population densities of other two carbide types are unaffected. Further tempering reduces the population density of SGCs in sub-zero treated steel, however, enhanced population density of these particles (as compared with CHT) is maintained, **Table 2**.

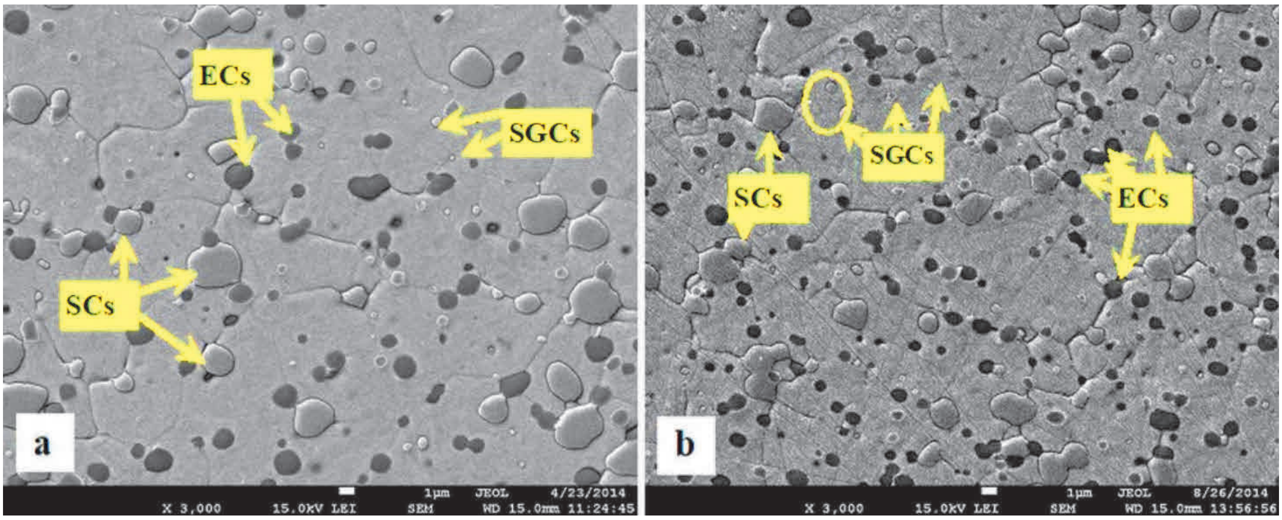

Figure 2 SEM micrographs showing the microstructure of the Vanadis 6 in untempered state, CHT (a), SZT (b)

Table 2 Population density of SGCs for CHT and SZT steel as a function of tempering temperature $[x10^{3}\ mm^{-2}]$

Tempering temperature [°C]	No	170	330	450	530
CHT	38.7 ± 1.2	33.5 ± 1.5	37.9 ± 1.6	37.6 ± 1.6	37.3 ± 0.8
SZT	147.9 ± 2.8	105.9 ± 2.1	98.8 ± 2.3	82.3 ± 4.0	79.2 ± 2.4

Potentiodynamic polarization curves, **Figure 3** clearly delineate the differences in corrosion behaviour of differently heat treated specimens. It is shown that sub-zero treatment leads to shift of corrosion potential to higher values (more anodic), and to lower corrosion current values. Tempering treatment, on the other hand, induces a shift of the corrosion potential towards lower values and higher corrosive currents. Thus, one can suggest that sub-zero treatment slightly improves the corrosion behaviour of the steel while tempering makes a worsening of corrosion resistance of the Vanadis 6 steel. Despite that, however, an improvement of corrosion characteristics were recorded for SZT steel compared to CHT one.

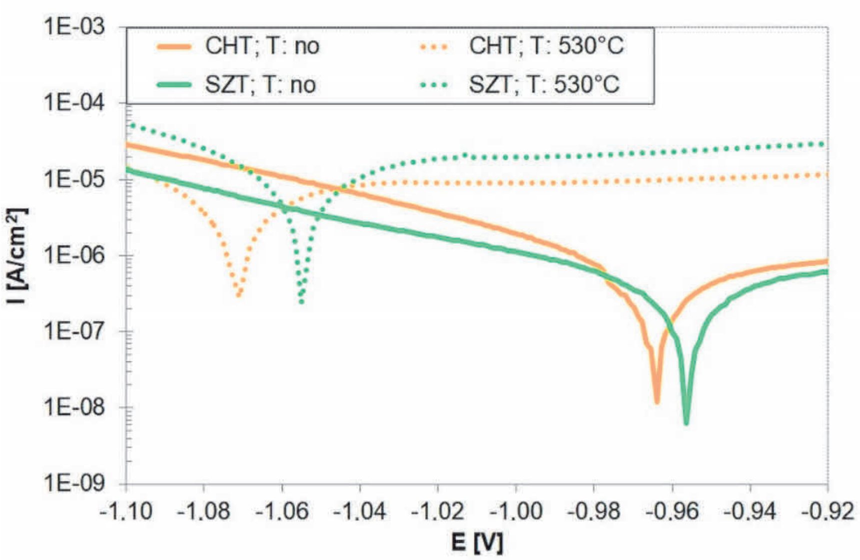

Figure 3 Potentiodynamic polarization curves after CHT (a) and after SZT at -196°C (b) in untempered state and in the state after tempering treatment 530°C

The corrosion rate (C_R) in dependence on the tempering temperature for CHT specimen as well as for the SZT ones is presented in **Figure 4**. It can be seen that the corrosion resistance decreases (corrosion rate increases).as the tempering temperature increases. Also it is obvious that SZT steel manifest better corrosion resistance (lower corrosion rate).

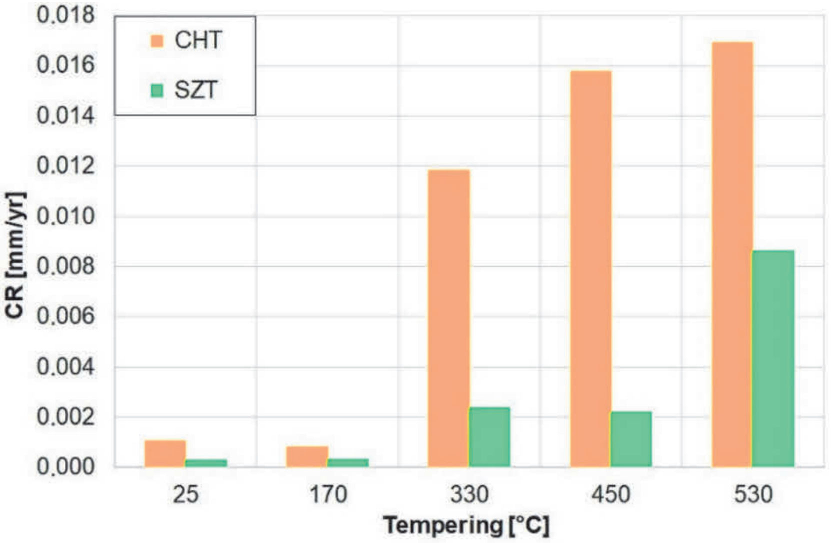

Figure 4 Corrosion rate in dependence on the tempering temperature for CHT and SZT steel

Figure 5 presents an example of SEM micrograph and corresponding EDS maps of the corrosion pit developed by the testing of SZT steel. As shown here, the matrix is relatively uniformly attacked by corrosion, where individual features of martensite are well visible. There are three types of carbides phases in the micrograph, namely eutectic carbides (ECs), secondary carbides (SCs) and small globular carbides (SGCs). It is obvious that the carbide/matrix interfaces manifest clear differences in the extent of corrosion attack. The matrix/SGCs interfaces are less extensively attacked while the interfaces of matrix with other (coarser) carbides manifest indications of very extensive corrosion attacks resulting in the extraction of particles from the steel sample.

4. DISCUSSION

The obtained experimental results suggest that the SZT improves the corrosion behaviour of the investigated tool steel. It should be mentioned here that the steel contains significantly reduced retained austenite amount after SZT (20.2 vs. 2.1 vol.% in the cases of CHT steel and SZT steel as reported recently [2]. In addition, SZT results in considerably enhanced amount and population density of small globular carbides, **Table 2**. These particles were identified as cementite [2, 3]. Improved corrosion resistance of SZT steel compared to CHT one appears counterintuitive with regard to reduction of retained austenite because it was experimentally proved that the austenite manifests more noble behaviour than the ferrite (or martensite) [9,10,11], as this phase is normally in weaker internal stress state, and that it contains lower amount of defects [12]. However, Villa et al. [13] and Ďurica et al. [14] reported high compressive stresses in the retained austenite, which may have beneficial effect on the corrosion resistance because of lowered interatomic spacing that facilitates the maintenance of the passivation films on the surfaces [15]. One can thus suggest that the state of high compression in the retained austenite after SZT can fully compensate the lower amount of this phase, with respect to its overall impact on the corrosion behaviour.

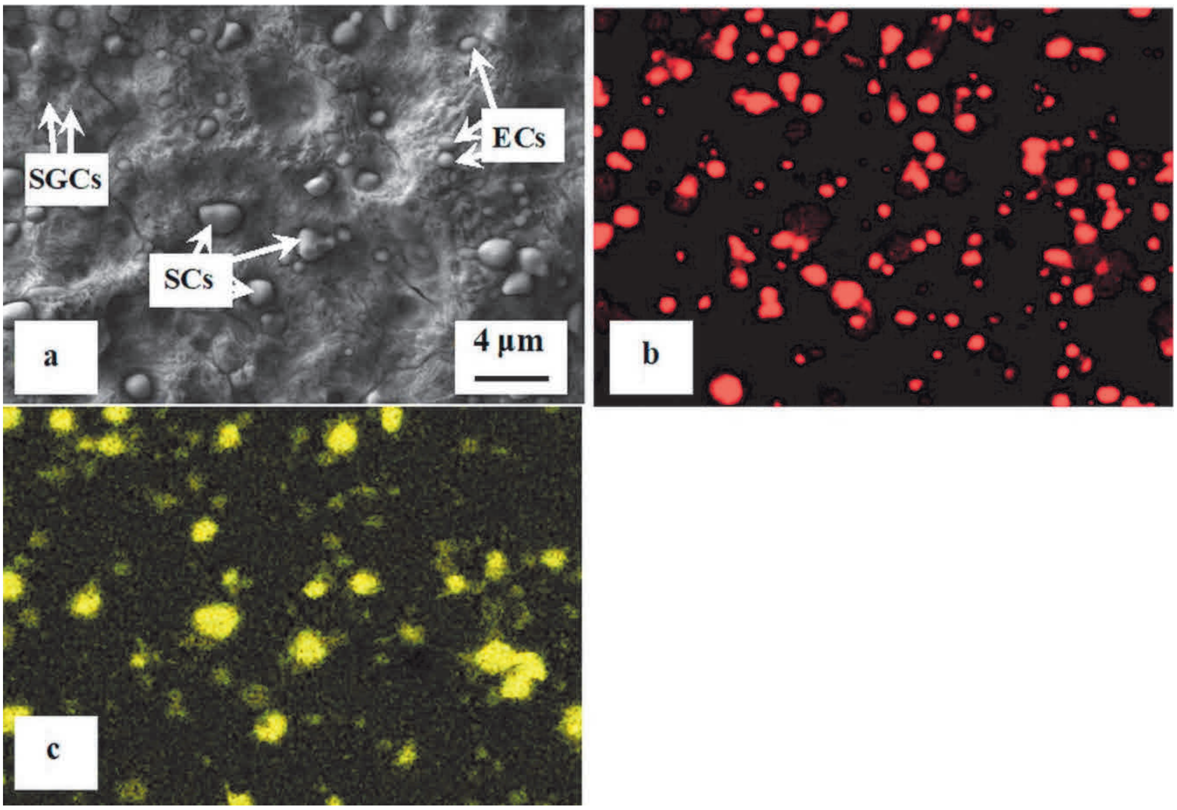

Figure 5 SEM micrograph showing the detail of corrosion pit (a), and corresponding EDS maps of vanadium (b) and chromium (c)

Also, one can expect rather worsening of corrosion behaviour of iron alloys with enhanced carbides amount. However, **Figure 5** clearly delineates that the extra SGCs are less attacked with corrosion than the other carbide particles. Moreover, it has been experimentally proved that the cementite manifested much nobler response on corrosion attacks than the solid solutions [16]. Based on that it can be stated that the presence of enhanced amount and population density of SGCs has rather positive affect on the corrosion behaviour of experimental tool steel.

Tempering induces a worsening of corrosion resistance. This is logical since it has been demonstrated recently [1,2] that this treatment promotes extensive precipitation of nano-sized carbides that depletes the matrix with chromium, hence, the protective passivation film on the surface becomes less stable, and thereby partly loses its ability to protect the material against corrosion.

5. CONCLUSIONS

Based on the presented results for the Vanadis 6 tool steel after SZT followed by tempering and their comparison with conventional heat treatment, the conclusions are as follows:

- Sub-zero treatment at the temperature of boiling nitrogen slightly improves the corrosion resistance of the Vanadis 6 steel in 3.5% NaCl water solution.
- Tempering treatment deteriorates the corrosion resistance of the material, however, slight improvement of corrosion behavior of SZT steel (as compared with CHT one) was maintained.
- Improvement of corrosion behaviour due to SZT can be attributed to high state of compression in retained austenite and to higher amount and population density of small globular carbides.

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