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Characterization of microstructure and tempering response of conventionally quenched, short- and long-time sub-zero treated PM Vanadis 6 ledeburitic tool steel

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ABSTRACT

The microstructure and tempering response of ledeburitic steel Vanadis 6 subjected to sub-zero treatments at a boiling temperature of liquid nitrogen for 4 and 17 h have been examined with reference to conventional heat treatment. The obtained results infer that i) sub-zero treatment induces time-dependent reduction of retained austenite amount, ii) the steel contains considerably enhanced population density of small globular carbides after sub-zero treatments; the population density is directly proportioned to the duration of sub-zero treatment, iii) application of sub-zero treatment results in overall refinement of the microstructure, iv) decomposition of retained austenite is accelerated by sub-zero treatments, v) tempering treatment reduces the population density of small globular carbides, vi) sub-zero treatments modify the precipitation behaviour of carbides; the precipitation of transient M_3C is accelerated within the low-temperature tempering range, but the precipitation of stable M_7C_3 carbides is rather suppressed within the normal secondary hardening temperature range, viii) the application of sub-zero treatment leads to complete loss of secondary hardening peak, ix) the overall tempering response of the Vanadis 6 steel is a result of competition between the tempering of the martensite, decomposition of the retained austenite, variations in the small globular carbides count, and precipitation of carbides; higher hardness of sub-zero treated and low-temperature tempered steel can be attributed to lower retained austenite amount, and much higher number of small globular carbides while the loss of secondary hardening peak is explained by much lower contribution of secondary martensitic transformation, suppressed precipitation of special alloy carbides, and reduced number of small globular carbides.

1. Introduction

Chromium-vanadium (Cr-V) ledeburitic tool steels are extensively used in modern tooling where high compressive strength and excellent wear resistance, along at least acceptable toughness are required. These materials are typical by high amounts of carbon, chromium and vanadium. Cr-V ledeburitic steels obtain their properties through proper heat treatment. The conventional heat treatment (CHT) consists of heating up to a temperature of stable austenite, hold at desired temperature followed by rapid quenching, and double (or triple) tempering. This heat treatment schedule results in a microstructure, which consists of tempered martensite, some retained austenite, undissolved carbides, and fine carbide precipitates.

The sub-zero treatment (SZT) is an add-on step to the CHT of high-carbon high-alloyed ledeburitic tool steels, whose austenite is not transformed to martensite after room temperature quenching in sufficiently high extent. In this step, the materials are immersed, immediately after quenching, into suitable cryo-processing media for a desired time and re-heated to the room temperature. After that, the tempering should be carried out, in order to reduce internal stresses formed due to the cooling, and to induce the transformations in the martensite and retained austenite (if any γ_R is presented in the microstructure). The tempering brings the steels the final bulk hardness, tensile/compressive strength, and the wear resistance.

In the 50s and 60s of the 20th century it was commonly believed that temperatures down to approx. -79 °C are sufficient to transform high portion of retained austenite into the martensite, and lower temperatures have no practical effect in treatment of steels. Besides the

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reduction of retained austenite, the effects like additional wear resistance, increased fatigue strength and better aging stability were accepted as the major advantages of SZT. Also, the acceptance a temperature of − 79 °C is a residue of some trials of heat treaters with 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, and obtained promising results.

Only much later, a temperature of − 196 °C was suggested for the treatment. The treatment at the boiling temperature of liquid nitrogen further increases the wear resistance of steels. For instance, laboratory test of the wear resistance of SZT AISI D2 steel showed an improvement by 316 and 817% when processed at − 79 and − 196 °C, respectively, despite the fact that the hardness manifested only a slight increase [1,2]. Real industrial trials with stamping- or powder compaction dies made of the same steel showed manyfold increase of tools durability [3,4].

The final properties of ledeburitic steels, which can be obtained by the tempering, are influenced by the initial state of the material, e.g. by the state achieved via either quenching or quenching and SZT. The ledeburitic steels contain the martensite (α'), the retained austenite (γ_R) and undissolved carbides after room temperature quenching as well as after sub-zero treatment [5]. The main differences between the microstructures of conventionally quenched ledeburitic steels and the sub-zero treated ones are the following:

i) The γ to α' transformation is more completed, thus, sub-zero treated Cr and Cr-V ledeburitic steels contain significantly reduced γ_R amount [6,7,8,9,10,11,16,17,18,19,20,21,22,23,24,25]. The authors differ one from each other only in the extent of the γ_R reduction – some of them claimed only significant reduction of the amount of this phase [6,10,16] while others reported almost complete removal of the retained austenite [8,11,17,18,19]. These contraindications might originate from several sources: different austenitizing temperature used for the investigations, different production route of the materials used (ingot metallurgy vs. P/M) etc. What is, however, also clear that the reduction of the retained austenite amount is temperature-dependent and time-dependent [8,11,17,19,26].

ii) The martensite of SZT steels manifests clearly evidenced refinement and it contains an enhanced number of lattice defects [6,10,27]. However, this is still a controversial issue. The following consideration can be used in order to clarify this phenomenon. It is noteworthy that the formation of the martensite during SZT is isothermal and not athermal (or diffusionless). However, one cannot expect any thermally activated atom transport at the cryo-temperature since it was earlier recognized that the carbon (and substitutional atoms, too) atoms are essentially immobile below approx. –50 °C [6]. Hence, the only possible way for the atoms to migrate at very low temperatures is through their capture and transport by gliding dislocations, which can be realized by plastic deformation, for instance. In other words, the plastic deformation of virgin martensite (note that virgin martensite formed at sub-zero Celsius temperatures is ductile in nature, and acquires its characteristic high strength, hardness and brittleness only in the course of reheating to the room temperature [28,29,30]) causes the dislocation movement, and this movement together with the transfer of certain carbon atoms would be responsible for controlling the growth of martensitic domains rather than the temperature effect.

The second possible effect being responsible for the refinement of martensitic domains can be designed as "spatial limitations in their growth". One can hypothesise that during conventional room temperature quenching, the martensitic domains grow relatively freely because there is much space for their growth available within original austenitic grains. On the contrary, the space for the growth of the martensite is very limited during the SZT since dominant portion of original austenite is already transformed into the martensite. As a logical consequence, the domains of the martensite formed during the SZT would be finer.

iii) Sub-zero treated ledeburitic steels can contain nano-sized precipitates of transient carbides, as a result of accelerated precipitation rate. However, this phenomenon is not entirely clear yet, also. It is only known that the tempering of high-carbon steels can be divided into several stages, namely the Stage I-II (pre-precipitation processes), Stage III (precipitation of transient carbides), and Stage IV (decomposition of retained austenite) [31].

In the 80s and 90s, several authors conducted extensive research focused to the investigation of the decomposition of high carbon Fe-C martensites, which were formed by either CHT or by SZT in liquid nitrogen. It is clearly seen that the opinions on the kinetics of the martensite decomposition are inconsistent; some authors claimed either "almost no effect" of the SZT on the decomposition kinetics [31,32,33] or retardation of the first decomposition stages [28] while others established rather accelerated decomposition rate of the martensite at low temperatures, due to lowered activation energy needed for this process [34,35,36].

For Cr-alloyed AISI D2 steel, Meng et al. [16] reported on accelerated precipitation rate of transient η - carbides owing to the SZT in liquid nitrogen. For the same steel grade, Pellizzari and Molinari [15] and da Silva Farina et al. [37] established a sequence of carbide phases formed during tempering, namely precipitation of transient carbides, cementite and special alloyed carbides around temperatures of 250, 500 and 600 °C, respectively.

Later, Gavriljuk et al. [38,39] published two more comprehensive studies focused to the precipitation of carbides in sub-zero treated P/M AISI D2 grade tool steel. They claimed that the precipitation of transient carbides is suppressed as a result of SZT, which was suggested to be associated with increased dislocation density in the martensite formed during SZT; enhanced dislocation density might retard the precipitation of transient carbides, due to a higher binding enthalpy between carbon atoms and dislocations compared with the formation enthalpy of these carbides [40]. However, these considerations manifest clear weak points. For instance, the authors are silent on the presence of small globular carbides (SGCs); enhanced number of these carbides was, however, reported recently for many different Cr and Cr-V ledeburitic steels [8,9,10,11,41]. It is unambiguous that the presence of these carbides has a clear impact on the composition of the martensite, and one can thus expect their impact on the precipitation behaviour of the nano-sized carbides. Further, the authors disregarded the effect of extremely enhanced compressive stresses in the retained austenite of SZT steels, see Ref. [27], which might act in favour of accelerated precipitation rate of carbides.

iv) Sub-zero treatment induces a formation of great number of so-called "small globular carbides" (SGCs). This fact was firstly observed by Collins et al. [18,42], and it was reaffirmed by many investigators more recently for the AISI D2 ledeburitic steel [8,11,20,43,44], AISI D6 steel [21], Vanadis 6 Cr-V ledeburitic steel [10,26], and AISI D3 ledeburitic steel [9,23,45,46]. Also, it has been demonstrated that mentioned increase is time- and temperature–dependent [8,9,11,12,26], and that these particles appear in the materials microstructure already before tempering [10,26]. The maximum population density of SGCs lies at the duration of SZT between 17 and 36 h, and likely correlates with the decrease in the retained austenite amount.

The impact of microstructural alterations on tempering response was first described by Berns [13]. He established that the SZT performed at − 196 °C for 15 min leads to shift of the secondary hardening