MICROSTRUCTURAL CHARACTERIZATION OF AN AISI D2 TOOL STEEL SUBMITTED TO CRYOGENIC TREATMENT[1]

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Abstract

Recent literature has shown several papers dealing with cryogenics treatments of tool steels. Most of them see an improvement in wear resistance supposedly due to microstructural modifications that occurs at cryogenics temperatures. Cryogenic treatments are supposed to modify the way secondary carbides precipitate, obtaining a finer and more homogeneous distribution. The present work discusses what is understood by secondary carbides and the modifications that occurs with micrometric (from the austenite-carbide field) and nanometric (from the temper of martensite) secondary carbides. No difference was found between the micrometrics carbides with and without cryogenic treatment, while some indications were found that the nanometric carbides are refined and more homogeneously distributed after cryogenic treatment. The samples were analyzed by Scanning Electron Microscopy.
Keywords: Cryogenic treatment; Temper carbides; Secondary carbides.

CARACTERIZAÇÃO MICROESTRUTURAL DE UM AÇO FERRAMENTA AISI D2 SUBMETIDO A TRATAMENTO CRIOGÊNICO

Resumo

A literatura recente tem apresentado diversos artigos sobre tratamento criogênico de aços ferramenta. A maioria deles apresenta melhoras na resistência ao desgaste, supostamente devido a modificações microestruturais que ocorrem em temperaturas criogênicas. Supõe-se que o tratamento criogênico modifica a forma de precipitação dos carbonetos secundários, obtendo uma distribuição mais fina e mais homogênea. O presente trabalho discute o que é entendido por carbonetos secundários e as modificações que ocorrem nos carbonetos secundários micrométricos (vindos do campo austenita-carboneto) e nanométricos (vindos da martensita revenida). Não foi encontrada nenhuma diferença nos carbonetos micrométricos com ou sem tratamento criogênico. No entanto, há indicações de que os carbonetos nanométricos são refinados e mais homogeneamente distribuídos após o tratamento criogênico. As amostras foram analisadas por Microscopia Eletrônica de Varredura.
Palavras-chave: Tratamento criogênico; Carbonetos de revenido; Carbonetos secundários.

1 INTRODUCTION

Cryogenic treatment has been shown to cause a large effect on the properties of heat treated steels, especially tool steels. However, the mechanisms proposed to explain the phenomena that occur during the holding time at cryogenic temperatures and in the following heating (up to room temperature or above) are not clear yet.

The main mechanisms proposed in the literature are: i) transformation of retained austenite in martensite;[1-3] ii) decomposition and conditioning of martensite;[3-5] iii) precipitation of eta (η) carbides[3,5] or an increase in its volumetric fraction.[4,6]

The sequence of solidification of an AISI D2 tool steel begins with the austenite formation followed by the eutectic reaction: $L \rightarrow \gamma + M_7C_3$, which characterizes the steel as hypoeutectic (in this work it will be utilized the carbides nomenclature presented by Boccalini and Goldenstein,[7] where primary carbides are the carbides precipitatet directly from the liquid and eutectic carbides are the carbides precipitated from an eutectic reaction) with the presence of M_7C_3 eutectic carbide cells in the as cast microstructure. The subsequent hot deformation of the ingots breaks down the eutectic carbide structure with intensity proportional to the degree of deformation.[8] When forging has been sufficient to break this cellular structure, coarse elongated eutectic carbides are distributed along the deformation direction. A finer distribution of spheroidized carbides precipitates in the solid state within the original grain matrix during cooling and also during the annealing treatment. Upset forging in these steels tends to partially eliminate the banded carbide structure and results in a more homogeneous distribution of the hard constituents.[9]

The initial microstructure for heat treatment usually is the annealed condition, with the matrix composed of ferrite containing globular carbides. During austenitization in the gamma + carbide field the secondary carbides precipitated during the cooling of the ingot and during annealing are partially dissolved, while simultaneously undergoing spheroidization and coarsening due to Ostwald ripening. All those phenomena occur before the cryogenic treatment.

The only opportunity for carbide precipitation after cryogenic treatment is during the tempering treatment. During tempering there is also carbide precipitation, but carbides precipitated during temper treatments are fine, abundant and uniformly distributed, with sizes between 30 and 70 nm.[10] Such secondary temper carbides precipitate preferentially along the laths of the martensite and are often coherent with the matrix, with well-established orientation relationships.[11] This work will focus in the temper treatments done after cryogenic treatment and at low temperatures (210°C).

According to Speich,[12] in medium carbon alloys, the temperature of 210°C can include the three first stages of tempering, that are: i) carbon segregation + precipitation of epsilon carbide; ii) decomposition of retained austenite; and iii) precipitation of a rod shaped cementite carbide. Hirotsu and Nagakura,[13] in a study with a martensitic high carbon steel, showed that the carbide precipitated at the first stage of tempering can be the eta carbide. According to then, the structure is similar but different from the hexagonal epsilon-carbide, as the eta carbide has a plate-like shape with thickness of 30-50 Å and precipitates periodically along dislocations, with an interval of about 100 Å. Similarly, Meng et al.,[5] proposed that the cryogenic treatment improves the preferential precipitation of fine eta-carbide instead of epsilon carbides, with the following mechanisms: "iron or substitutional atoms expand and contract, and carbon atoms shift slightly due to lattice deformation as a result of cryogenic treatment".

Recently, Das et al.,[14] published papers using AISI D2 tool steel, were they found an increase on the population density and on the size of the "secondary" carbide particles with cryogenic treatment followed by tempering at 210°C, and they associate to it an improvement in the wear resistance.[15] However, the so called secondary carbides in their work are in the range of 0.1-1 μm, which is the size of carbides present in the gamma+carbide field, at the austenitizing temperature; there is no possibility that those alloy carbides (M_7C_3) could dissolve or precipitate at cryogenic temperatures or even at low temperature tempering, as substitutional diffusion would be needed. A possible explanation could be that the microstructural changes described by then are an observation artefact, since their initial microstructure has an intrinsically heterogeneous carbide distribution. Their micrographs show that the eutectic carbide structure (ledeburitic) left over from the solidification is still visible; the rounded secondary carbides are probably precipitated in the solid state during the cooling of the ingot, and spheroidized during austenitization in the gamma + carbide field. From the microstructures they present we can infer that the reduction during hot forging of the bars were not enough to distribute evenly the eutectic carbides and consequently to remove the composition heterogeneities arising from the solidification process. Although they mention in the articles the presence of such primary carbides (here called eutectic carbides), they state that this is not a problem as all the samples have the same eutectic carbides volume fraction and they do not change during the heat treatment.[14]

In face of such unexpected results, the aim of the present work is to reproduce Das et al.[14] heat treatments, using as initial material D2 steel bars with more homogeneous distribution of carbides. In order to do that, the volume fraction of micrometrics carbides before and after the cryogenic + tempering treatment was measured. Also the micro/nanomicrostructure of the carbides precipitated at tempering was thoroughly characterized utilizing Scanning Electron Microscope.

2 MATERIALS AND METHODS

The experiments were carried out with samples of a VD2 cold work tool steel, conventionally ingot casted and hot rolled to the diameter of one inch with degree of deformation around 90 times. The steel was produced at Villares Metals S.A. (Sumaré – Brazil) and the chemical composition is presented on Table 1.

**Table 1.** Chemical composition of a VD2 tool steel, weight %, Fe - balance

C	Mn	Si	Cr	V	Mo
1.51	0.36	0.35	11.9	0.78	0.73

Samples from the VD2 tool steel bar (cut from mid radius of the bar) were submitted to different thermal treatment cycles, following the cycle done by Das et al.[14] The samples were austenitized at 1020°C for 40 minutes and then quenched in oil to room temperature. One of then was tempered (210°C/2h x2) just after the oil quench. The other three had an intermediate cryogenic treatment between quench and temper. The cryogenics treatments were: i) -196°C/36 h; ii) -125°C/10min; iii) -75°C/10 min. The choice of 10 minutes instead of 5 like Das et al.[14] is due to the absence of control on the cooling rate of our apparatus, and the need to guarantee time enough to homogenise the temperature at the part. The samples were identified as shown in Table 2.

Table 2. Identification of the samples with respective cycle of heat treatment

Sample	Thermal Cycle
C1	1020°C/40min (↓oil)
C10	1020°C/40min (↓oil) + 210°C/2h (x2)
C3	1020°C/40min (↓oil) + (-196°C/36h) + 210°C/2h (x2)
C6	1020°C/40min (↓oil) + (-125°C/36h) + 210°C/2h (x2)
C9	1020°C/40min (↓oil) + (-75°C/36h) + 210°C/2h (x2)

For the measurement of the volumetric fraction of carbides, the samples were conventionally prepared: they were ground with SiC sand paper and polished until 0.5 µm Alumina. Chemical etching was done with Villela reagent. The samples were analyzed by SEM; For quantitative analysis of the carbide volume fractions and distribution of sizes BSE-SEM images of unetched samples were used, with2000x magnification. For each sample 3 micrograph images were analyzed using Image J software. The process of analysis with Image J software, described in Figure 1 was: (a) from the original image file, (b) the image file were converted to binary color and the fraction of carbide measured by the corresponding area. Different sizes of carbides were separated and analyzed individually (Figure 1c to 1f). With these results for the three images for each sample, the histogram of size distribution and the volumetric fraction of carbides were obtained.
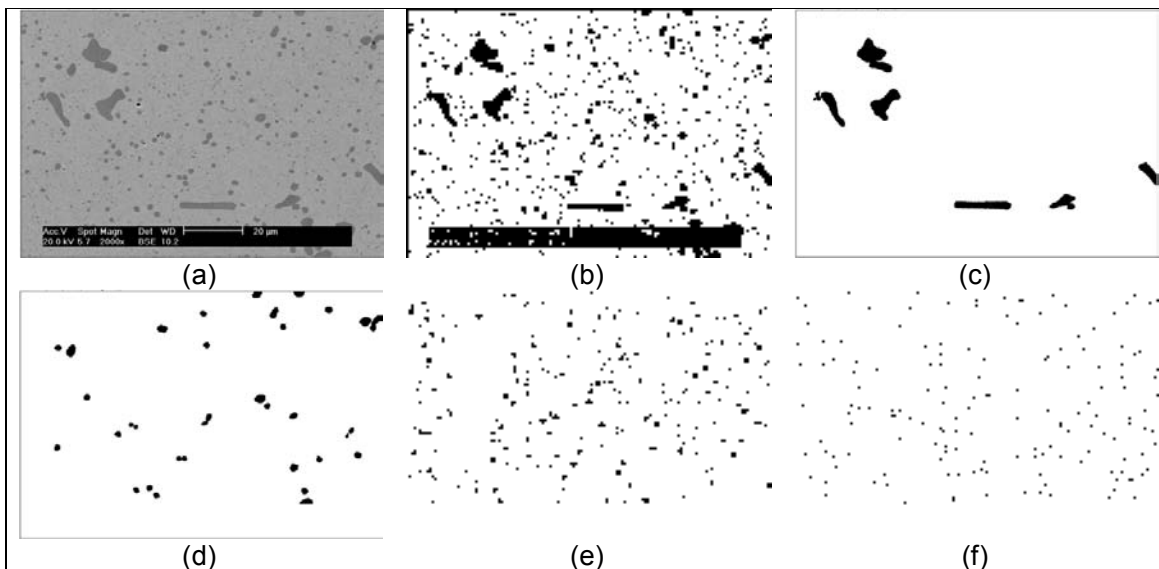
Figure 1. Sequence used for determining volumetric fraction of carbides with the software ImageJ. (a) original microstructure – SEM; (b) binary image; (c) mask showing the carbides size bigger than 5µm; (d) mask showing the carbides sizes between 1-5µm; (e) mask showing the carbides sizes between 0.1-1µm; (f) mask showing the carbides/noise (maybe just an artifact) lower than0.1µm.
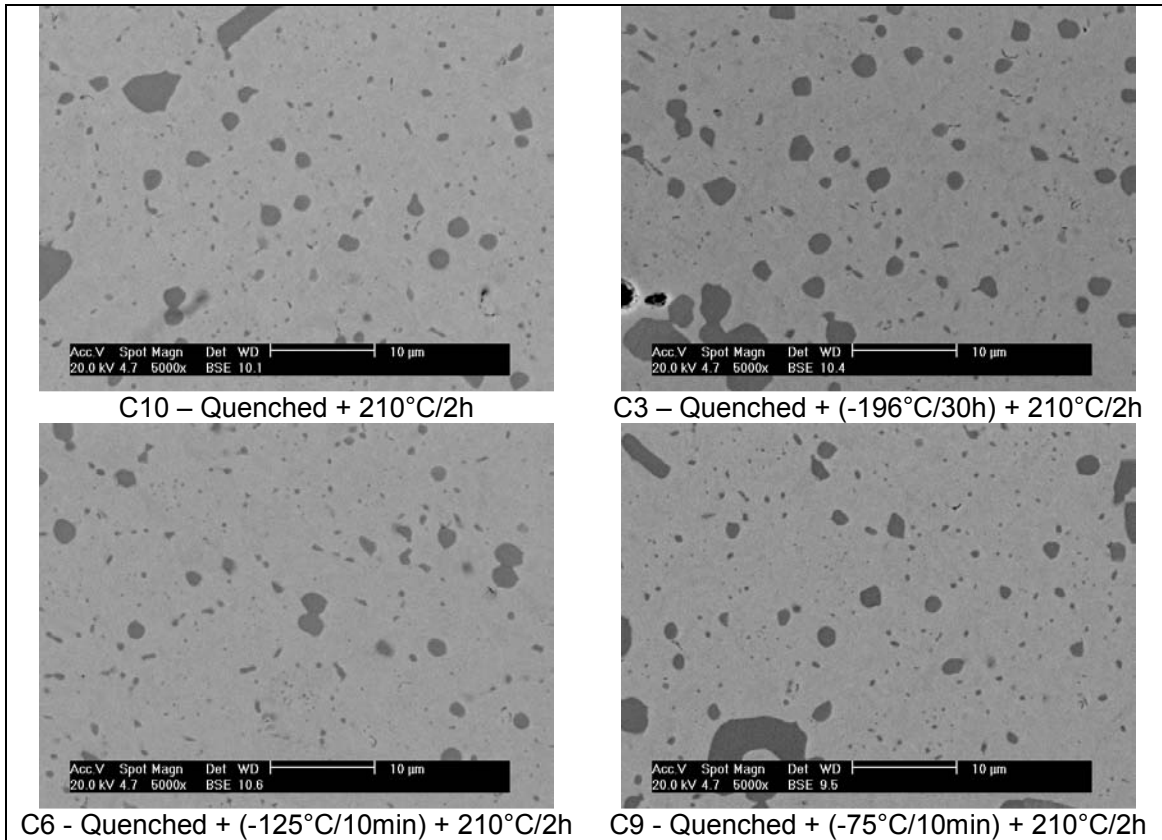
For the metallographic characterization of the types of carbides, the samples were etched with Villela for 10 seconds, and analyzed by SEM with the utilization of image of secondary electrons (SE).

3 RESULTS

Figure 2 presents the microstructure of the samples analyzed by SEM with SE image; it is possible to see eutectic and secondary carbides. The samples utilized for the measurement of volumetric fraction carbides was with lower magnification to

avoid the artefacts due to the distribution of the eutectic carbides, as higher is the magnification, more heterogeneities from big particles are taken. The choice for the samples without etching for the volumetric fractions was due to the effects that the etching could cause to the results: i) higher volumetric fractions due to the bigger apparent area of carbides; and ii) lower volumetric fraction, especially from the small carbides, if they are pulled out with the etching.

| C10 – Quenched + 210°C/2h | C3 – Quenched + (-196°C/30h) + 210°C/2h |
| C6 - Quenched + (-125°C/10min) + 210°C/2h | C9 - Quenched + (-75°C/10min) + 210°C/2h |

Figure 2. Microstructure of specimen C3, C6, C9 and C10. Not etched. SEM-BSE.

Figure 3 presents the volumetric fraction of carbides, divided by range of sizes: i) larger than 5 µm; ii) between 1 and 5 µm; iii) between 1 and 0.1 µm; and iv) lower than 0.1µm. The last one (lower than 0.1µm) is not a totally reliable value, because it is possible that the presence of background noise affects the results. From those results it is clear that there is no difference between cryogenic treated and plain samples with regard to volume fraction of carbides, both eutectic and secondary, within the range of size verified. The big error bar found for the eutectic carbides (bigger than 5µm) is due to the magnification utilized, which was focused in the smaller carbides. No efforts were done to measure the eutectic carbides with an appropriate magnification or utilizing a larger number of fields. For the other sizes of carbides, there are no differences between samples that underwent different thermal cycles. It is clear then that the evaluated carbides are not precipitated after the cryogenic treatment or during/after tempering because all the volumetric fractions are the same as for the sample C1 that is "as quenched".
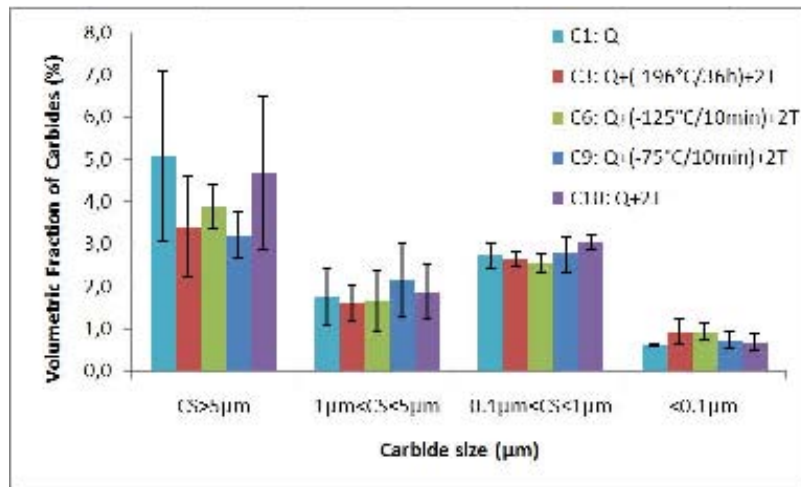
Figure 3. Volumetric fraction of the different sizes of carbides from samples C1, C3, C6, C9 and C10. Bar error for a 95% confidence interval.

Figure 4 shows the microstructures of the samples after tempering (C10, C3, C6, C9). It is possible to note the presence of nanometric carbides in addition to the micrometric carbides. Sample C10, without the cryogenic treatment, was the only one with the presence of retained austenite (visible at SEM) after the temper, showing that the cryogenic treatment was efficient to eliminate the austenite.
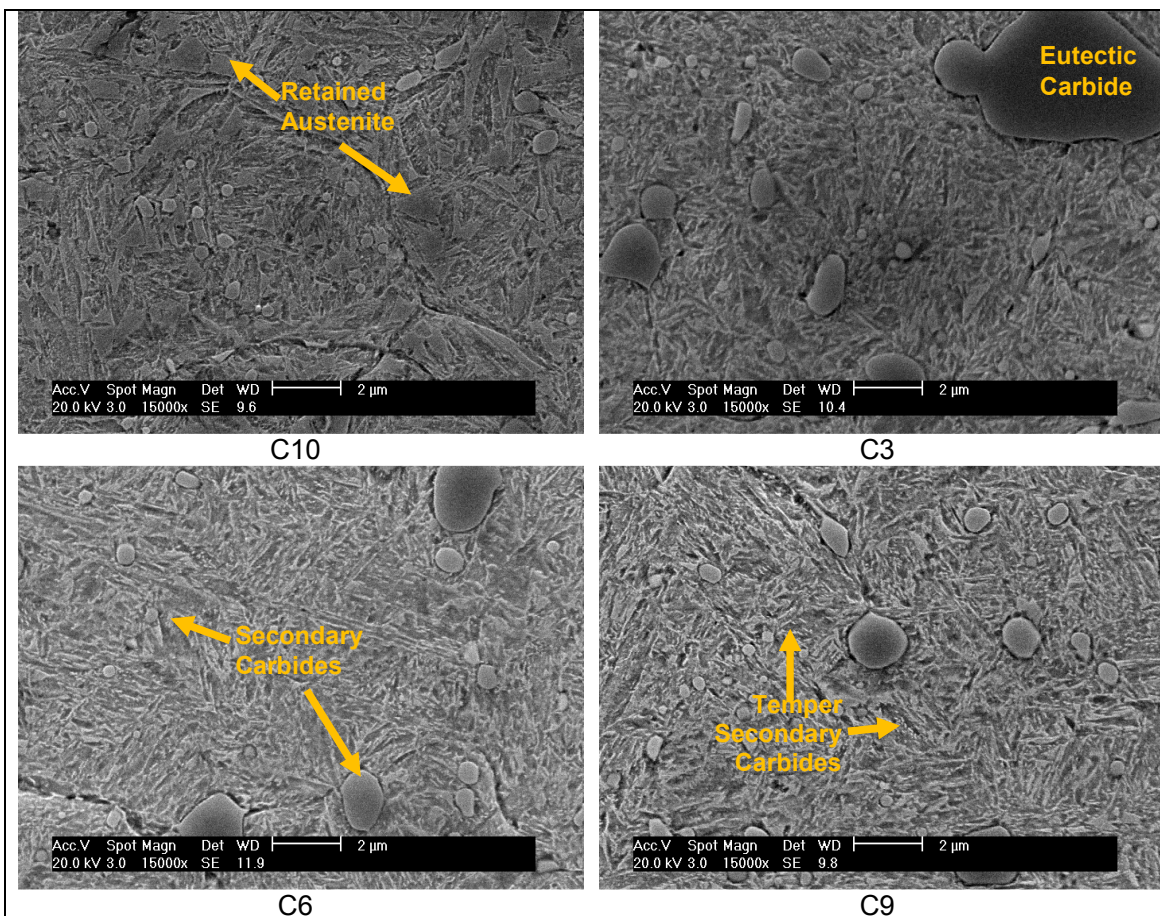

Figure 4. Microstructure of specimen C3, C6, C9 and C10, showing: (C10) retained austenite; (C10, C3, C6 and C9) the eutectic and nanometric temper carbides. Etching: Villela/10s. SEM-SE.

Figure 5 presents in detail the micro/nanostructures of the sample C6. It is possible to see clearly the nanocarbides precipitated during the tempering, delineating the laths of former martensite and the secondary carbides.

Figure 6 presents in detail the micro/nanostructures of the sample C10, without cryogenic treatment. It is possible to see the retained austenite, the secondary carbides, the nanocarbides precipitated during the tempering and the retained austenite (blocky structures).
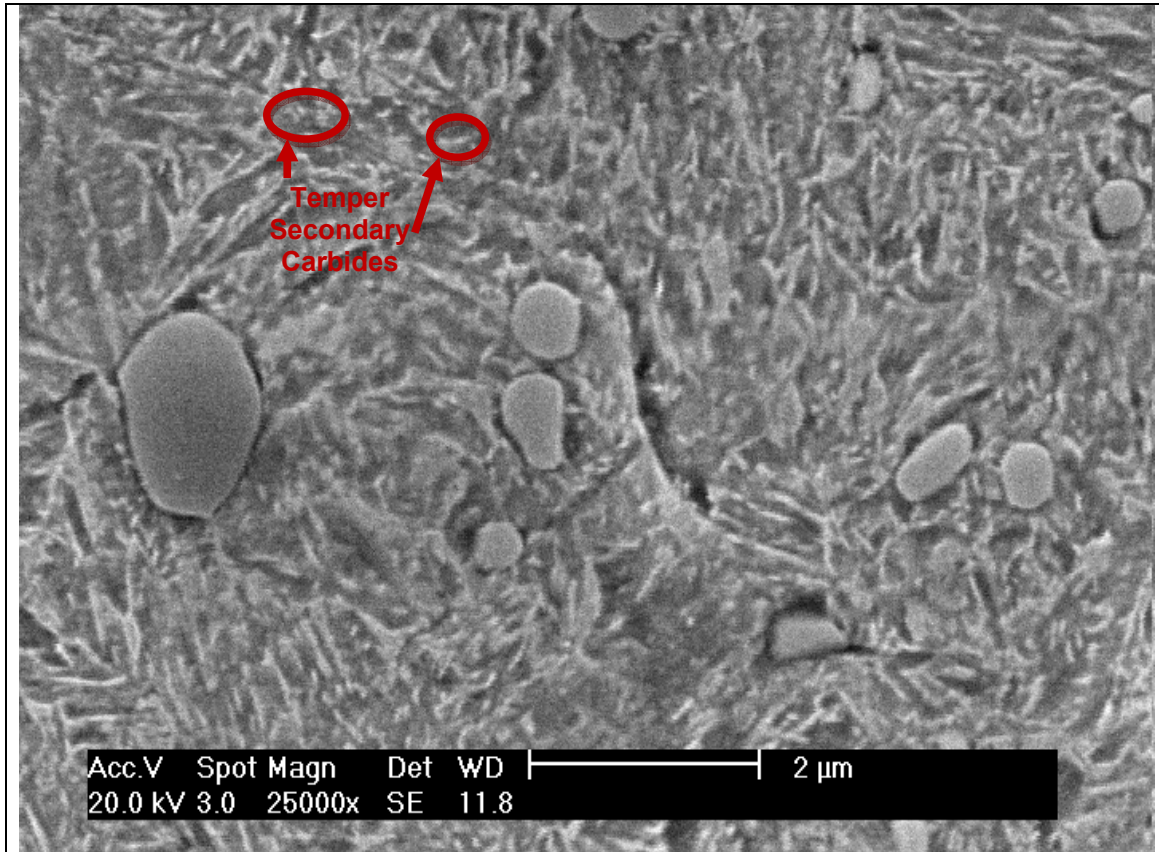
Figure 5. Detail from the microstructure of the sample C6, showing the nanometric temper carbides, delineating the former martensitic structure. Etching: Villela/10s. SEM-SE.
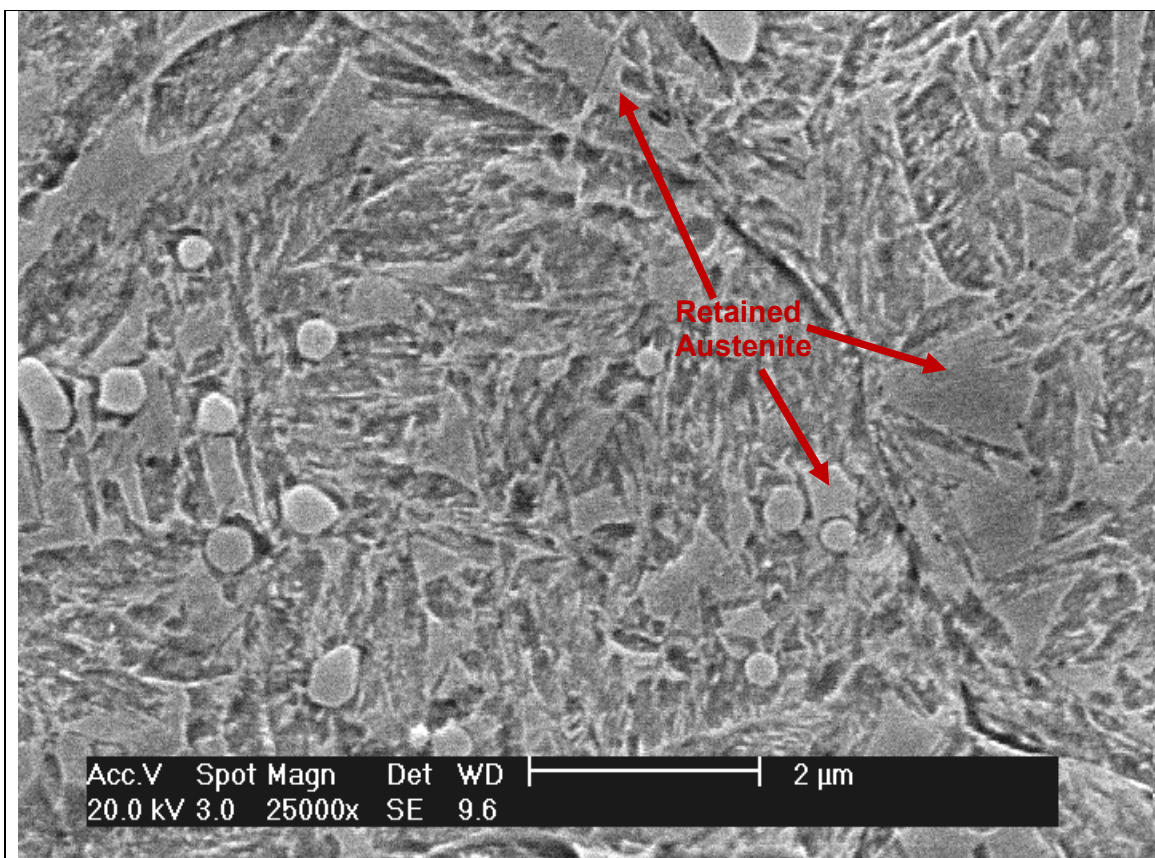
Figure 6. Detail from the microstructure of the sample C10, showing the retained austenite (blocky), the eutectic carbides and nanometric temper carbides, delineating the former martensitic structure. Etching: Villela/10s. SEM-SE.

From Figures 5 and 6 could be said that the cryogenic treatment cause a difference in distribution of the secondary temper carbides, however, this difference could not be quantified: the secondary temper carbides seems to be longer in Figure 6, indicating a refining of the nanostructure in the cryogenic treated samples.

4 DISCUSSION

The cryogenic treatments at -75°C, -125°C and -196°C were effective to transform the retained austenite to martensite as could be seen by SEM-SE image (Figures 4, 5 and 6). However, in the present work, the retained austenite was not measured, so it is not possible to state that there is no retained austenite remaining in the microstructure of the cryogenic treated samples.

The present work showed that for the micrometric secondary carbides, precipitated from the austenite + carbides field, there is no difference in the volumetric fraction or in the size with the insertion of a stage of cryogenic treatment in the thermal cycle. This is in deeply disagreement with Das et al.,[14] they assert that the sub-zero treatments refine such carbides, increasing their amount and leading to a more uniform distribution in the microstructure.

The apparent increase in the population and refinement of the nanocarbides precipitated from temper is in good agreement with the work of Meng et al.[5] and Dong et al.[4] Dong et al.,[4] stated that the ultrafine carbides precipitated out in the cryogenic treatment grow larger during subsequent tempering, but are apparently

smaller in size and more evenly distributed than the ones found after conventional heat treatment.

The bigger population of temper carbides in the cryogenic treated samples could be related to the fact that there is no retained austenite in such samples. The sample without cryogenic treatment has retained austenite between the laths of martensite – that can not be seen by SEM - and, it was found retained austenite in blocks along the microstructure of the sample. The austenite is able to retain more carbon in solution than the martensite, in this way, limiting the volume of carbides that can be formed during tempering.

5 SUMMARY

The cryogenic treatment does not change the volume fraction or distribution of the secondary carbides that are micron sized and precipitate directly from the austenite.

The cryogenic treatment showed to be effective in the reduction of retained austenite.

There is an apparent increase in the population and a refinement of the nanometer-size carbides (temper carbides) when a cryogenic stage is introduced in the thermal cycle.

There is confusion in the literature concerning the types of carbides that can be possibly modified by the introduction of a cryogenic treatment between quench and temper: only nanometer size, metastable temper carbides can be possibly modified by the cryogenic treatment.

Acknowledgements

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