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ON THE INFLUENCE OF DEEP CRYOGENIC TREATMENT ON TEMPERING TRANSFORMATIONS IN AISI D2 STEELS

Massimo Pellizzari¹, Vasco Menegante¹, Matteo Villa², Marcel A. J. Somers²

1 University of Trento, Department of Industrial Engineering, Via Sommarive 9, 38123 Trento, Italy

2 Technical University of Denmark, Department of Mechanical Engineering, DK 2800 Kongens Lyngby, Denmark

massimo.pellizzari@unitn.it, vasco.menegante@studenti.unitn.it, matv@mek.dtu.dk, somers@mek.dtu.dk

The aim of this paper is to investigate the effect of deep cryogenic treatment (DCT) on the tempering behaviour of AISI D2 steel. Dilatometry samples were austenitized at 1030°C for 30min and thereafter quenched at 120°C/min. One set of samples was isochronally tempered at a rate of 6°C/min until 800°C to distinguish four tempering stages: i. precipitation of transition carbides (RT-220°C), ii. precipitation of cementite (220-350°C), iii. decomposition of retained austenite (600-650°C) and iv. precipitation of secondary alloy carbides (450-700°C). In-situ Synchrotron X-Ray Diffraction (S-XRD) investigation of the same tempering cycle shows a reduction of the martensite tetragonality in stage i. In stage ii., retained austenite experiences a marked lattice expansion, which can be ascribed to relaxation of phase-specific compressive stresses (stresses of type II) that had built-up during quenching. Stages iii. and iv. start at approx. 450°C with C depletion of retained austenite, as revealed by an anomalously low thermal expansion of the austenite lattice at $T > 450^\circ\text{C}$, and continues with a further relaxation of the martensite structure starting at 540°C. Simultaneously, austenite decomposes into ferrite and secondary alloy carbides, which is completed at 650°C. The effect of DCT, carried out by immersion in boiling nitrogen and soaking at -196°C for various times, can be summarized in a) a shift of transition carbide precipitation to higher temperature, b) a more pronounced volume reduction associated with precipitation of cementite and c) a less pronounced volume expansion associated with (partial) decomposition of RA. Very limited effects (if any) of storage time in boiling nitrogen (i.e. 5min vs 29 h or 72 h) could be observed on dilatometry curves and on the structural parameters of austenite and martensite.

KEYWORDS: TOOL STEEL - CRYOGENIC TREATMENT - RETAINED AUSTENITE – DILATOMETRY – DIFFERENTIAL SCANNING CALORIMETRY - XRD - SYNCHROTRON

INTRODUCTION

Deep Cryogenic Treatment (DCT) of tool steel is considered an effective way to improve the life of tools and dies. The literature documents many application studies that report a dramatic improvement in wear resistance and mechanical properties after introducing low temperature soaking at boiling nitrogen temperature (-196°C) of steels, in particular ledeburitic cold work tool steels like AISI D2 [1-3]. DCT has the largest impact when the steel microstructure comprises freshly formed (untempered) martensite, retained austenite and undissolved eutectic carbides. It should therefore be carried out immediately after quenching from the austenitization temperature. Then, the most evident and directly measurable effect of DCT is the transformation of (most of) retained austenite into martensite, causing a hardness increase [4]. Nevertheless, martensite formation alone cannot account for the positive effect of DCT on the performance. Consequently, less evident and controversial effects, challenging metallurgical principles, have been reported for the effect of DCT. It is the authors' opinion that a deeper metallurgical understanding of the influence of DCT on the steel microstructure is of primary importance to enable targeted and reproducible performance.

The phase transformations occurring during tempering in plain carbon steel and in low- and medium alloyed steels have been described in the literature and comprise i) the precipitation of transition carbides from martensite, ii) the decomposition of retained austenite into ferrite and cementite and iii) the precipitation of cementite from transition carbides and segregated carbon [5]. Furthermore, pre-precipitation stages including C atom redistribution by segregation and clustering at low temperature (<100°C) were reported. Segregation of C atoms to lattice defects and grain boundaries

reduces the C content in solid solution in martensite. Clustering is a local enrichment of C atoms, which may act as a preferential nucleation site for transition carbide precipitation.

For highly alloyed steels, like ledeburitic cold work tool steels, the three classical stages are slightly modified, mostly because substitutional alloy elements (Cr, Mo and V) shift all transformations to higher temperature and lead to secondary carbide precipitation at about 500-550°C. Hence, cementite becomes a transition carbide that, after precipitation at low temperature, is replaced by secondary alloy carbides. The tempering sequence in these tool steels involves i) the precipitation of transition ϵ -carbides from martensite [6], ii) the precipitation of cementite from transition carbides and segregated carbon, iii) the decomposition of retained austenite into ferrite and cementite [7] and iv) the precipitation of secondary carbides like M_7C_3 , $M_{23}C_6$, MC and M_2C , from Cr, V and Mo, respectively [6,8]. All the above phase transformations can be conveniently, albeit indirectly, studied by combining differential scanning calorimetry and dilatometry [5,9], considering that events accompanied by large enthalpy changes may correspond to small volume changes and vice versa. DCT has been shown to enhance the pre-precipitation step which leads to increased carbide precipitation from martensite during tempering [10,11]. According to [11] it has been shown that longer DCT soaking times lead to a higher degree of transformation of RA into martensite, as well as more clustering and segregation of carbon, which promotes carbide precipitation.

The aim of this paper is to investigate the effect of DCT on the tempering behaviour of AISI D2 steel. Dilatometry, differential scanning calorimetry and in situ synchrotron X-Ray diffraction (S-XRD) were applied to study the influence of storage in liquid nitrogen for different times on the stages of tempering.

MATERIALS AND EXPERIMENTAL PROCEDURES

A commercial AISI D2 cold work tool steel (1.55%C, 0.3%Si, 0.4%Mn, 11.3%Cr, 0.8%Mo, 0.8%V) was used for this research work.

Cylindrical samples (\varnothing 4mm, length 10mm), were extracted by electro-discharge machining from a cylindrical bar (\varnothing 12mm) with main axis along the rolling direction. All heat treatments were carried out using a Bähr 805A/D dilatometer. Samples were austenitized at 1030°C for 30min followed by quenching (Q) at 120°C/min. One set of samples was isochronally tempered at a rate of 6°C/min until 800°C to distinguish the four tempering stages. Three sets of samples were deep cryogenically treated immediately after quenching by immersion in boiling nitrogen (-196°C) and soaked for 5min (0h), 29h and 72h (DCT0, DCT29 and DCT72). Final (rapid) heating to RT was achieved by immersion of the samples in a beaker containing ethanol. Analogous to the Q samples, the DCT samples were isochronally tempered at a rate of 6°C/min until 800°C. Tempering started within 15min after reaching RT, to avoid retained austenite stabilization. For all conditions, additional samples were isochronally tempered using a differential scanning calorimeter (model Perkin Elmer DSC7). Discs (\varnothing 4 mm, 50-80mg) were cut from quenched dilatometry samples with a precision micro-cutting machine with a mounted diamond blade. Lubrication and a very low feed rate were used to avoid any possible stress/strain-induced transformation of austenite. In view of the limited enthalpy change associated with phase transformations, two scans were carried out on each sample. Assuming that all phase transformations were completed after the first scan, the second curve was used for background subtraction from the first scan. The complete list of samples (dilatometry, DSC and S-XRD) and related symbols is reported in Table 1.

The fractions of retained austenite in the un-tempered Q and DCT samples was determined by XRD analysis using $Co K\alpha$ radiation. The measurements were performed in the 2θ range of 40°–110°, using a step size of 0.1°2 θ , with a counting time per step of 5 s. The volume fraction of retained austenite was calculated by the Rietveld method using MAUD (Materials Analysis Using Diffraction) software. For microstructural analysis of these conditions scanning electron microscopy (SEM) was used after standard metallographic preparation, using emery papers and diamond paste. The 0.1 kg Vickers hardness was measured according to ASTM-E92.

Energy dispersive in situ Synchrotron X-Ray Diffraction (S-XRD) investigation of the same isochronal tempering cycle was performed several weeks after hardening at the synchrotron facility HZB-BESSY II at the experimental station EDDI [12]. Samples were 0.3mm thick disks \varnothing 12mm. Austenitization (1030°C, 30min) was performed in a horizontal Kanthal tube furnace under a continuous Ar flow and was followed by quenching (average rate of ~25°C/min, ~120°C/min in the interval 550°C-1030°C). DCT consisted of immersion of the samples in boiling nitrogen, soaking at -196°C for 72h and re-heating to room temperature by immersion in water. DCT was performed immediately after quenching. Tempering was performed in an Anton Paar DHS 1100 Domed Hot Stage under Ar atmosphere (continuous flow, 1.4 bar). The samples were placed on the heating element (alumina plate) onto which they were secured by mild clamping. The temperature

was measured with a Pt-Pt10Rh thermocouple fixed to the stage. Diffraction lines were fitted with pseudo-Voigt profile functions. The evolution of the fraction of retained austenite during tempering was evaluated from the relative intensity of the 200_{γ} , 311_{γ} and the $200_{\alpha'}$, $211_{\alpha'}$ reflections for austenite and martensite, respectively. The relaxation of the martensite structure was evaluated based on the Integral breadth β (and on the asymmetry, not presented here) of the $200_{\alpha'}$ reflection. The lattice parameter of austenite was evaluated from the positions of the 200_{γ} and 311_{γ} reflections on the energy scale. A gold reference standard was used for calibration of the absolute value of the lattice parameters.

Table 1 – Heat and cryo treatments for the investigated samples

HEAT and CRYO treatment				
Sample code	Quenching – Q		Deep Cryogenic Treatment – DCT	Hardness HV0.1
Q	1030°C	0.5 h	-	905±20
Q+DCT0	1030°C	0.5 h	-196 °C for 5 min	911±5
Q+DCT29	1030°C	0.5 h	-196 °C for 29 h	945±10
Q+DCT72	1030°C	0.5 h	-196 °C for 72 h	952±13

RESULTS AND DISCUSSION

As quenched (Q) and cryo-treated (Q+DCT) samples

The microstructures of Q, Q+DCT0 and Q+DCT72 samples show a martensitic matrix containing a high fraction of Cr rich M_7C_3 eutectic carbides (Figure 1). Due to the limited resolution, scanning electron microscopy cannot resolve the finest microstructural details regarding the influence of DCT. These are currently under investigation with transmission electron microscopy. According to thermodynamic calculations, the C content in austenite is 0.55 wt%, which would correspond to a mixture of $\{557\}_{\gamma}$ lath and $\{225\}_{\gamma}$ plate martensite forming below M_s (145°C). Also, the formation of a very small amount of bainite was detected on the dilatometry diagram. Moreover, S-XRD revealed the presence of MC and $M_{23}C_6$ carbides after hardening. The austenite content, determined by XRD, is about 12vol.% in Q and decreases to about 4-5 vol.% after DCT. The hardness increases from 905 to a maximum of 952HV0.1 (Tab. 1).

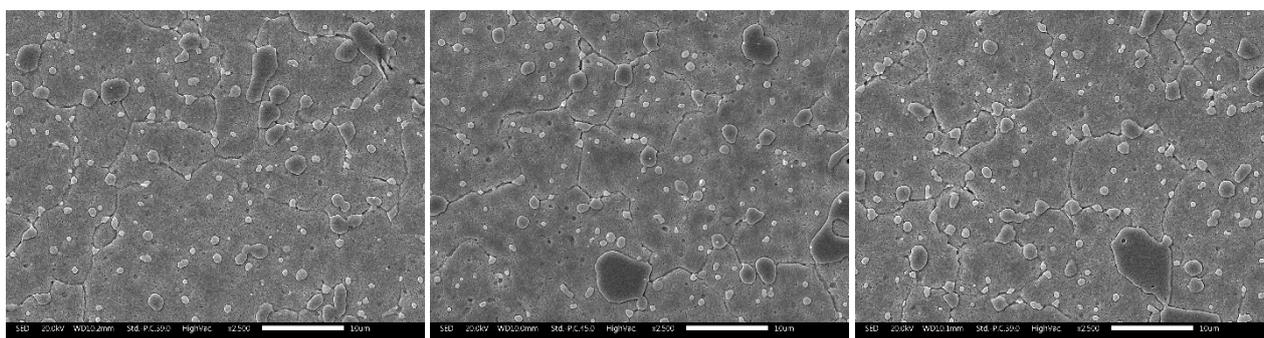


Fig.1 – Secondary electron images of the microstructure of Q, Q+DCT0 and Q+DCT72 (left to right).

Tempered samples

The isochronal tempering behavior of Q is described in Figure 2. The first derivative of the dilatometry strain (black curve) highlights four peaks that, consistent with literature, can be ascribed to the following transformations:

- I. precipitation of transition carbides (RT-220°C)
- II. precipitation of cementite (220-350°C)
- III. decomposition of retained austenite (600-650°C) and
- IV. precipitation of secondary alloy carbides (450-700°C).

All precipitation reactions are accompanied by a volume contraction, while the decomposition of retained austenite into ferrite and alloy element carbides leads to an expansion. In-situ S-XRD investigation of the same tempering cycle shows a relaxation of the martensite structure from tetragonal to cubic in stage I, as demonstrated by (not shown here)

asymmetric-to-symmetric evolution of the martensite peaks, reflected by a marked reduction of the Integral breath of the $200_{\alpha'}$ reflection (blue dots in Fig. 2). In stage II, retained austenite experiences a marked lattice expansion (red dots in Fig. 2), which can be ascribed to relaxation of phase specific compressive stresses in austenite (stresses of type II) that had built-up during martensite formation [13]. Conversely, in the temperature range 450°C-650°C, the austenite lattice (red dots in Fig. 2) shows an anomalously low coefficient of thermal expansion (CTE), which indicates that, concurrent with thermal expansion, a volume reduction occurs; perhaps by gradually reducing the C content. Note in this respect the small peaks on the dilatometry curve in-between II and III, suggesting precipitation reactions. Finally, on continuous heating, retained austenite (green dots in Fig. 2) decomposes into ferrite and secondary alloy carbides (stage III) at a slightly higher temperature and the reaction is completed at 650°C. Eventually, a further relaxation of the tempered martensite structure commences at 540°C along with the precipitation of alloy carbides and the decomposition of retained austenite (stages III and IV).

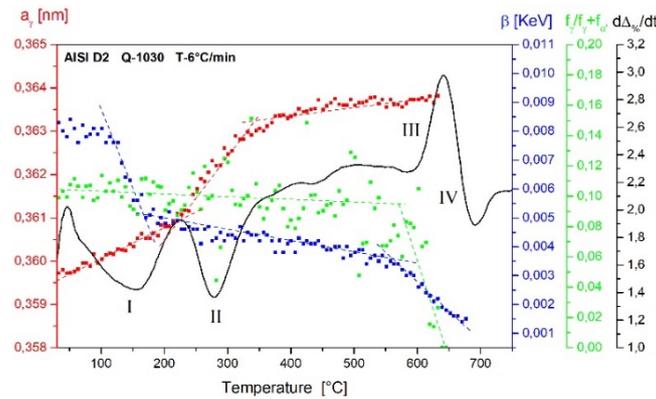


Fig.2 – Isochronal tempering diagram of Q sample: first derivative of dilatometry strain (black), integral breath of the $200_{\alpha'}$ martensite peak in S-XRD (blue), austenite fraction (green) and austenite lattice parameter (red).

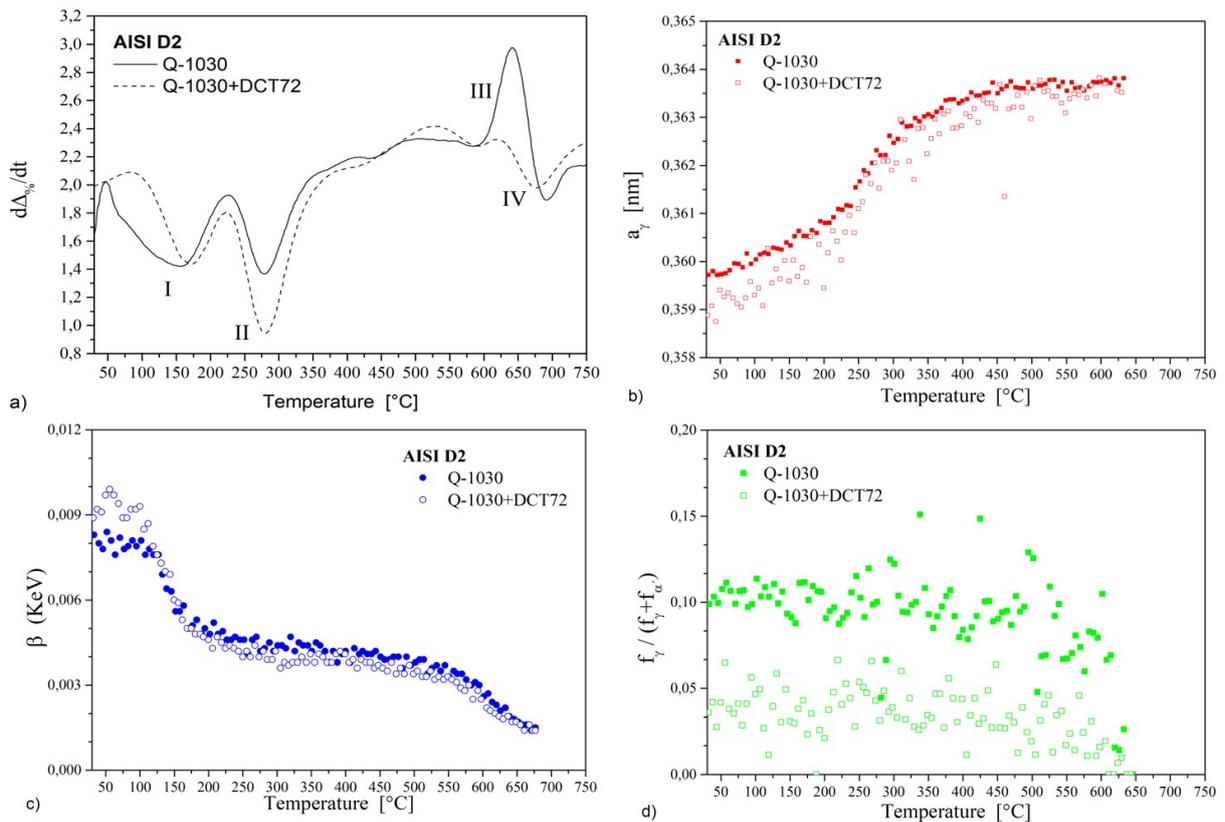


Fig.3 – Isochronal tempering diagram of Q-1030 and Q-1030+DCT72: a) first derivative of dilatometric strain, b) austenite lattice parameter, (c) integral breath of the $(200)_{\alpha'}$ martensite peak and d) austenite fraction.

Based on dilatometry, the following observations are made comparing Q and DCT72 (Fig. 3a):

- CTE is slightly reduced after DCT72 as compared to Q, because more martensite is present;
- the onset of transition carbide precipitation in stage I is shifted to higher temperature after DCT72;
- the volume reduction associated with precipitation of cementite (stage II) from martensite is more pronounced;
- the volume expansion associated with (partial) decomposition of RA (stage III) is less pronounced.

Moreover, S-XRD on Q and DCT72 appears to evidence a systematically, albeit slightly, lower lattice parameter of retained austenite (indicating higher compressive stress) up to its decomposition temperature (Fig.3b), a higher tetragonality of martensite (larger β) before the completion of transition carbides precipitation (up to 120°C, Fig.3c) and a lower amount of austenite (Fig.3d) for Q-DCT72 vs. Q.

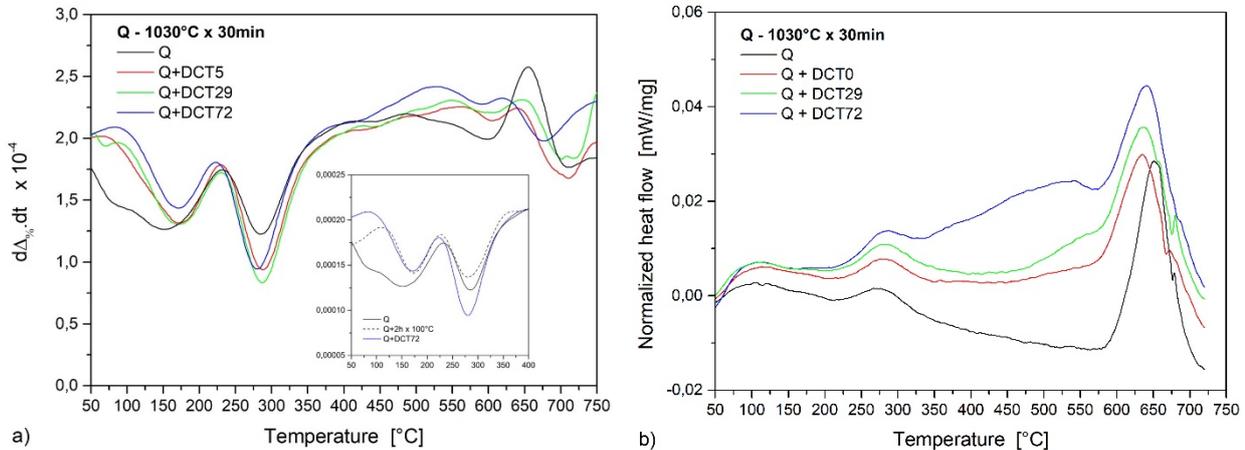


Fig.4 – Isochronal tempering diagram of Q and Q+DCTx samples: a) first derivative of dilatometric strain, b) DSC heat flow. Inset in Fig. 4a shows the dilatometric curve of a sample quenched and tempered for 2h at 100°C.

Apart from the anticipated effects associated with a lower retained austenite fraction, the most striking result seems to be the shift of stage I to higher temperatures after DCT. In view of the higher content of martensite and structural defects introduced by DCT (i.e. dislocations), precipitation would be expected at least at the same temperature as for Q, most likely at a lower temperature. A more detailed view of the Q dilatometry signal suggests that peak I is the result of a two consecutive contractions and that the low temperature contribution disappears after DCT. To further investigate this effect, one sample was quenched and tempered at 100°C for 2h. Its dilatometry curve (inset in Fig.4a) confirms that the contraction up to 100°C is now lacking and that only the contribution above this temperature remains. In view of the almost perfect superimposition with the peak of Q+DCT72, it is concluded that low temperature transformation occurs during DCT. It is anticipated that the contraction below 100°C is due to a pre-precipitation stage and, in particular, to the segregation of carbon atoms to lattice defects, because clustering does not cause a significant volume decrease [14]. This is in agreement with the large amount of dislocations introduced in lath martensite by DCT [15]. On the other hand, the higher intensity of the cementite precipitation peak and the sheer disappearance of the austenite decomposition in Q+DCTx samples are directly related to the martensitic transformation at low temperature. In relation to the soaking time at -196°C, dilatometry curves suggest that the time of storage in boiling nitrogen (i.e. 5 min, 29 h or 72 h) has a limited effect, if at all, on the tempering behaviour of AISI D2 (Fig. 4a). In fact, the same conclusions drawn for Q+DCT72 (points a-b) can be extended to DCT0 and DCT29. Nevertheless, a systematic increase in CTE in the temperature interval 450°C-550°C with longer soaking time is observed along with shifts of the small peaks in this temperature range. This suggests a modification of the precipitation reactions with soaking time. Further investigation is needed to clarify the origins of these peaks.

DSC curves (Fig. 4b), displaying the enthalpy changes related to the various phase transformations, show a marked influence of DCT and the soaking time at -196°C. After prolonged storage time in LN the signals become more and more exothermic (curves are rotated anticlockwise), particularly at higher temperature. Considering that these are subtracted curves, this effect can be interpreted with a lower exothermic contribution during the second run: in other words, due to the slower kinetics of transformations occurring at higher T and the limited time available during isochronal tempering, transformations cannot complete during the first run and do it during the second one [16]. Prolonged DCT appears to

improve the transformations during the first tempering. This effect appears to be active from low temperature: the first exothermic shoulder observed below 100°C, corresponding to C clustering [5] is enhanced by DCT. Apparently, in the temperature range of transition carbide precipitation (80-220°C) no peak is observed in DSC: this is plausibly due to the relatively low enthalpy change associated to this precipitation and the partial overlap with clustering at lower temperature and with cementite precipitation at higher temperature. Cementite precipitation (peak II) is enhanced by DCT, in agreement with dilatometry. Because of the strong overlap, the peaks related to retained austenite decomposition (peak III) and secondary carbide precipitation (peak IV) cannot be distinguished easily. Along with the higher amount of retained austenite in Q, a stronger exothermic peak could be expected. On the other hand, the crystallographic parameters of martensite and retained austenite (Fig.3) do not provide evidence for structural differences to justify such a different behaviour for Q and Q+DCTx samples. New DSC measurements are ongoing to further investigate these effects.

CONCLUSIONS

The influence of DCT on the phase transformations occurring during tempering of AISI D2 was investigated. Independently from the storage time in LN (5min, 29h and 72h), DCT causes the partial transformation of retained austenite and a hardness increase. Furthermore, the coefficient of thermal expansion is reduced as compared to the quenched material and the volume expansion associated with decomposition of RA is less pronounced, because more martensite is present. For the same reason, the volume contraction due to cementite precipitation from martensite is more pronounced. A final important effect of DCT is the shift of the onset of transition carbide precipitation to higher temperature. Preliminary results confirm that storage in LN leads to the disappearance of a volume effect below 100°C on tempering, which would imply that segregation of carbon to lattice defects has occurred prior to tempering. DSC indicated an effect of the storage time at -196°C during DCT on the kinetics of the precipitation reactions in-between stages II and III.

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