

Influence of RT soaking on the stability of retained austenite in 72NiCrMo4 tool steel

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Tool steels are used in a wide range of manufacturing applications including the automotive field. Their heat treatment implies a rigorous scheduling to avoid scarce properties and reliability related problems. Stabilization of retained austenite (RA) due to prolonged soaking between martensite start (Ms) and finish (Mf) leads to its more difficult transformation during tempering or even after subzero treatment.

Aim of this research is to analyse the influence of different room temperature soaking periods (0, 5, 120h) on the stabilization of RA and the effect of an additional deep cryogenic treatment (DCT, -196°C, 30min) before tempering in a 72NiCrMo4-2 cold work steel. A set of samples has been isochronally tempered just after quenching, so to avoid RA stabilization. Dilatometry highlighted the three classical tempering stages, namely the precipitation of transition carbides (100-200°), the decomposition of retained austenite (250-300°C) and the precipitation of cementite from transition carbides and segregated carbon (200-450°C). DCT carried out just after quenching causes the almost complete transformation of RA, so that the expansion accompanying the II tempering stage was suppressed. The RT soaking stabilizes RA such that even DCT is no more sufficient to achieve a fully martensitic structure. Furthermore, the stabilization process also affects the early the tempering stages, in particular the precipitation of transition carbides.

KEYWORDS: TOOL STEEL – CRYOGENIC TREATMENT – TEMPERING – DILATOMETRY – DIFFERENTIAL SCANNING CALORIMETRY - RETAINED AUSTENITE.

INTRODUCTION

Low alloyed cold work steels are interesting materials for the production of tools (circular cutting blades, knives...). After proper machining tools are quenched leading to a steel microstructure consisting of primary martensite, retained austenite and, eventually, undissolved carbides. The fraction of austenite mostly depends on the C content, which in turn depends on the redissolution degree of carbides during austenitizing. The stability of austenite, i.e., its capability to be transformed into ferrite and carbides during tempering, is also largely determined by its chemical composition as well as by its stabilization during any room temperature aging between quenching and tempering. It's widely known that a long time RT exposure before tempering (i.e. between martensite start Ms and finish Mf) makes the austenite decomposition more difficult [1]. Cold treatment (CT, T > -80 °C) and Deep cryogenic treatment (DCT, T << -80 °C, typically at LN temperature, -196 °C) were firstly introduced to help the martensitic transformation of austenite, in view of the larger and larger driving force obtained far below martensite start (M_s) temperature. In this sense, these treatments could be also considered as a powerful healing method to transform RT stabilized austenite. Furthermore, DCT has been claimed to be an effective way to induce a finer and more homogeneous precipitation of secondary car-

bides during tempering resulting in higher hardness (due to the transformation of RA into martensite) and improved wear resistance [2,3].

The phase transformations occurring in low and medium alloyed steels during tempering have been extensively described in literature. The three classical stages are i) the precipitation of transition carbides from martensite, ii) the decomposition of retained austenite into ferrite and cementite and iii) the

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precipitation of cementite from transition carbides and segregated carbon. Furthermore, pre-precipitation stages including C atoms redistribution by segregation and clustering at low temperature (<100°C) were reported. Clustering of C atoms is a local enrichment C atoms, which may act as preferential nucleation site for transition carbide precipitation. Segregation allows C atoms to leave the matrix to be associated to lattice defects and grain boundaries.

All the above phase transformations can be conveniently studied by combining differential scanning calorimetry and dilatometry [4,5], considering that events associated to large enthalpy changes may correspond to small volume changes



Their cumulative effects are a net volume expansion and a large heat evolution. The conversion of transition carbides into cementite is accompanied by a large volume contraction and a large heat evolution, which are strongly superimposed to the signals related to the austenite decomposition.

The influence of RT aging has been considered in [6,7] showing that it leads to C redistribution by clustering, thus anticipating what would happen during tempering immediately after quenching. In general, segregation at RT is much less important in steels showing high enough M_s , because big part of segregation (up to 0.2%wt C) can occur still during quenching. The stabilization of austenite was confirmed by the inability of a deep cryogenic treatment in liquid nitrogen (the immersion time is not reported in [4]) to (fully) transform this phase after 24h aging at RT [4]. The effect was much less evident after an ageing time of 5h only, confirming that the

and vice versa. Clustering does not cause any change of the unit cell volume or the lattice parameters of martensite, while it was associated to a low temperature shoulder in DSC curves. On the other hand, segregation leads to a decrease of unit cell volume and a limited enthalpy change [4]. Precipitation of transition carbides causes a large length decrease and an appreciable heat evolution. The transformation by which retained austenite (γ_R) decomposes into ferrite (α) and cementite (θ) (Eq.1) may be seen as the result of two separate stages including the intermediate formation of a high C austenite (Eq.2) and its final decomposition into ferrite and cementite (Eq.3) [6]:

aging time may play an important role with this respect. DCT (immersion in LN for 8 and 24h) has been shown to enhance the pre-precipitation step which leads to increased carbide precipitation from martensite during tempering [8]. According to this study it was proved 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 promote carbide precipitation.

In this study a series of experiments has been carried out to study the influence of RT soaking on the austenite stability in a low alloyed cold work tool steel. The study also investigates if this phenomenon can be eliminated, or at least mitigated, by deep cryogenic treatment (DCT). Dilatometry and differential scanning calorimetry have been used to evaluate the effects of RT stabilization time and DCT on the tempering transformations.

MATERIALS AND EXPERIMENTAL PROCEDURES

The material tested is a cold tool steel, 72NiCrMo4-2 (AISI 8670, 1.2703mod.), with the composition reported in Table 1.

Tab. 1 - Chemical composition of steel (wt%)

TABLE HEADING								
	%C	%Si	%Mn	%P	%S	%Cr	%Mo	%Ni
Min	0.710	0.226	0.483	0.008	0.008	0.380	0.069	0.780
Max	0.720	0.235	0.486	0.008	0.011	0.380	0.069	0.79

Cylindrical samples (length $l=10$ mm, diameter $\phi=4$ mm), were obtained by mechanical machining from a rolled sheet along the longitudinal direction. All heat treatments have been carried out using a Baehr dilatometer, model 805A/D. Quenching (Q) was carried out heating up the samples to

900°C at 30°C/min, maintaining the samples at the maximum temperature for 15 minutes, then cooling to room temperature at 100 °C/s by means of a high pressure N2 flow. The influence of retained austenite stabilization on its decomposition during heat treatment was studied by performing

Heat treatment

an isochronal tempering at 10 °C/min up to 500 °C, after different aging times at room temperature (RT0h, RT5h and RT120h). The dilatometric strain data were mathematically averaged over time and subsequently differentiated by temperature, in order to define the different transformation peaks during tempering. For each soaking time two quenched specimens were prepared, one of which further underwent deep cryogenic treatment by direct immersion in liquid nitrogen at -196 °C for 30 min before being tempered. The complete list of treatments and samples is reported in Table 2.

All samples were also isochronally tempered at 10 °C/min up to 500 °C using a differential scanning calorimeter (model

Perkin Elmer DSC7). DSC samples (discs $\varnothing=4$ mm, 50-80mg) were cut from quenched dilatometric samples by precision microcutting machine mounting a diamond blade. Lubrication and a very low feed rate were used to avoid any possible stress/strain induced transformation of austenite.

Microstructural analysis was carried out by scanning electron microscopy (SEM) after standard metallographic preparation using emery papers and diamond paste. The amount of retained austenite was determined by XRD analysis using a Cu radiation. The HV1 hardness was measured according to ASTM-E92.

Tab. 2 - Heat treatments with the relative symbols

TABLE HEADING			
Sample code	Q	RT soaking time	Cryogenic treatment
Q	900°C at 30 °C/min	-	-
Q+DCT	900°C at 30 °C/min	-	-196 °C for 30 min
Q+RT5h	900°C at 30 °C/min	5 h	-
Q+RT5h+DCT	900°C at 30 °C/min	5 h	-196 °C for 30 min
Q+RT120h	900°C at 30 °C/min	120 h	-
Q+RT120h+DCT	900°C at 30 °C/min	120 h	-196 °C for 30 min

RESULTS AND DISCUSSION

The dilatometric curve recorded during quenching shows the formation of martensite only, starting from 201 °C (M_s), suggesting that some auto-aging can occur still during quenching [7]. The positive slope of this curve at RT further indicates that the martensitic transformation is incomplete (Figure 1).

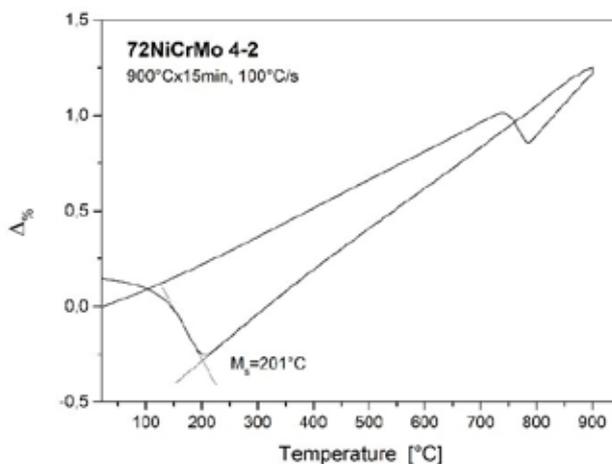


Fig. 1 - Dilatometric curve recorded during quenching

X-ray diffraction analysis (Figure 2) allowed to determine about 7%RA. Accordingly, the Q sample shows a martensitic microstructure with polygonal areas of retained austenite situated between α' platelets (Figure 3) and some isolated undissolved carbides. The hardness is of 872 ± 6 HV1.

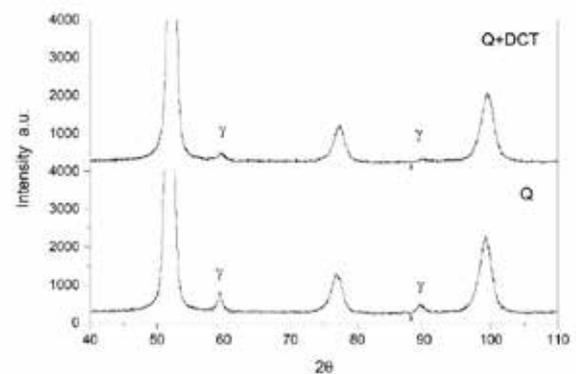


Fig. 2 - XRD spectra of Q and Q+DCT samples

DCT immediately after quenching promotes the partial transformation of RA: despite of the very low cryogenic temperature, about 4%RA is found in Q+DCT sample (Figure 2), confirming the inability of DCT to fully transform RA. According

to Villa this could be explained by the very fast cooling rate during direct immersion in liquid nitrogen [9]. The hardness of Q+DCT is of 930 ± 5 HV1.

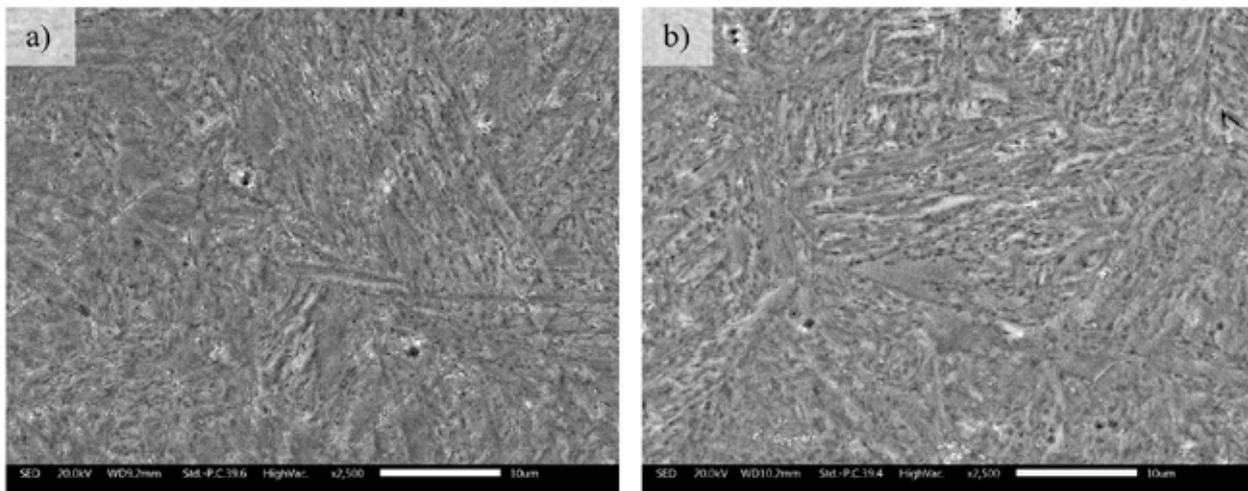


Fig. 3 - SEM micrographs of **a)** Q and **b)** Q+DCT samples

Tempering after quenching (Q) and DCT (Q+DCT)

Dilatometric and DSC curves (Figure 4) highlight the stages occurring during isochronal tempering of steel in the as quenched state Q. According to literature [1-4-7], these can be ascribed to the following phase transformations:

Peak I (150°C): Precipitation of transition carbides in martensite

Peak II (280°C): Decomposition of retained austenite

Peak III (330°C): Precipitation of cementite

Precipitation stages (I and III) are accompanied by a volume contraction, while the decomposition of austenite (II) by a net volume expansion (Fig.1a). The superimposition between peaks II and III is well evident, so that their opposite volume change makes them distinguishable. The same transformations are accompanied by exothermic signals, the most intense being that related to the austenite decomposition (Fig.1b). Moreover, DSC evidences a low temperature shoulder ($T < 80^\circ\text{C}$) due to Carbon redistribution: in particular,

considering the C content of present steel (0.7%wt) and that a large part of segregation (0.2%C) may occur still during quenching, clustering is held to be responsible for this effect [4,6,7].

The effect of DCT can be summarized with a more intense precipitation of transition carbides and the (almost complete) transformation of austenite, as confirmed by the absence

of dilatometric peak II and the lower intensity of peak II in DSC. The disappearance of dilatometric peak II highlights that the contraction due to the precipitation of cementite already starts at 220°C and corroborate the assumption that peak II in DSC is not uniquely associated to austenite decomposition. Clustering is also enhanced by DCT (see the shoulder in DSC), as found by one of authors for a similar steel [8]. This stronger clustering is in agreement with the stronger transition carbides precipitation shown by dilatometry (segregated C does not take part to transition carbides precipitation).

Heat treatment

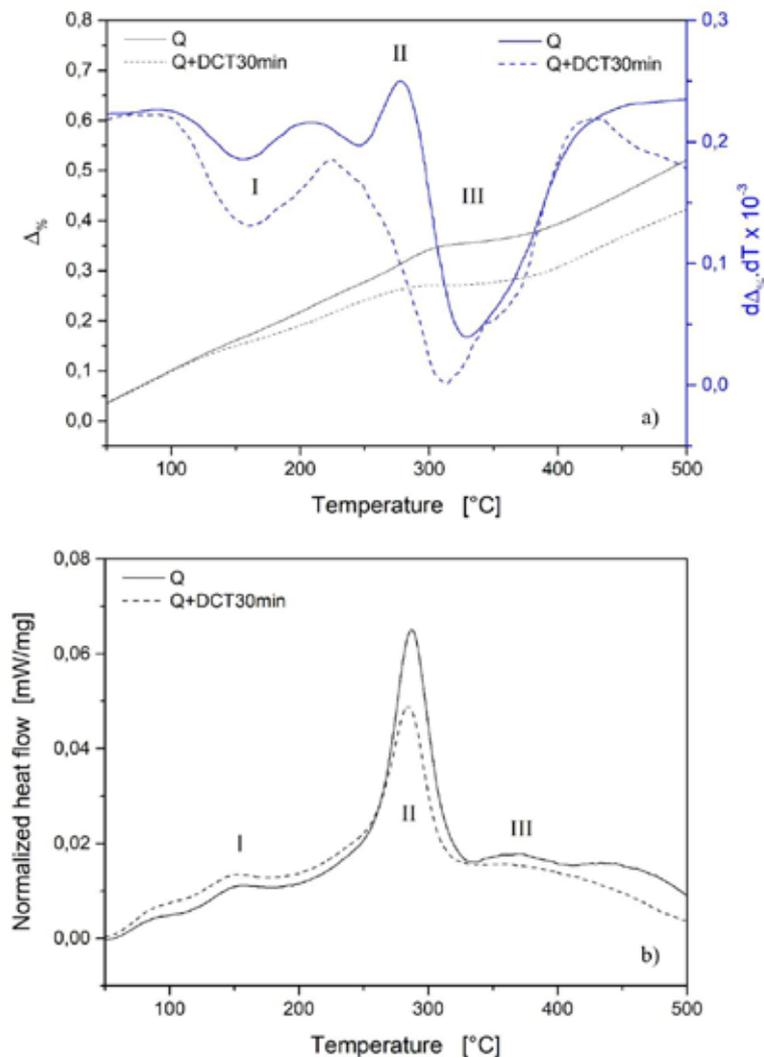


Fig. 4 - a) Dilatometric curves and **b)** DSC curves for Q and Q+DCT samples

The above results are in agreement with the transformation of a large fraction of retained austenite into martensite during DCT. The higher amount of α' will therefore lead to an enhanced precipitation of transition carbides in the first stage of tempering and enhanced cementite precipitation in the third stage.

One more effect of DCT seems to be an anomalous small expansion at about 340°C, which does not correspond to any appreciable DSC signal: to the authors best knowledge this effect has not been described before and could be associated to an extra-precipitation (compared to Q) of segregated C to cementite [4]. This could be explained with the higher dislocation density introduced by DCT [10]. Alternatively, it could be also related to some further retained austenite sta-

bilization that survived to DCT. According to Villa [11], the additional martensite transformed during the -196°C soaking produces some localized volume increase that puts the RA under a compressive stress, causing this phase to need a larger driving force to complete its transformation on tempering. As described in the introduction the RA decomposition during tempering (Eq.1) has been described as a two-step process (Eq.2-3). It is plausible that DCT may affect them, causing the dilatometric peak associated to the second transformation to be shifted towards higher temperatures. Other phenomena not completely explainable, like secondary carbides precipitation, or even non-detectable by dilatometry may be involved, and further investigation would therefore be needed.

Tempering after RT aging (Q+RTx) and DCT (Q+RTx+DCT)

Figures 5a-b display the influence of 5 and 120h RT soaking on the tempering behaviour of present tool steel, by

dilatometry and DSC, respectively. For purpose of comparison the curve of Q sample is also re-reported.

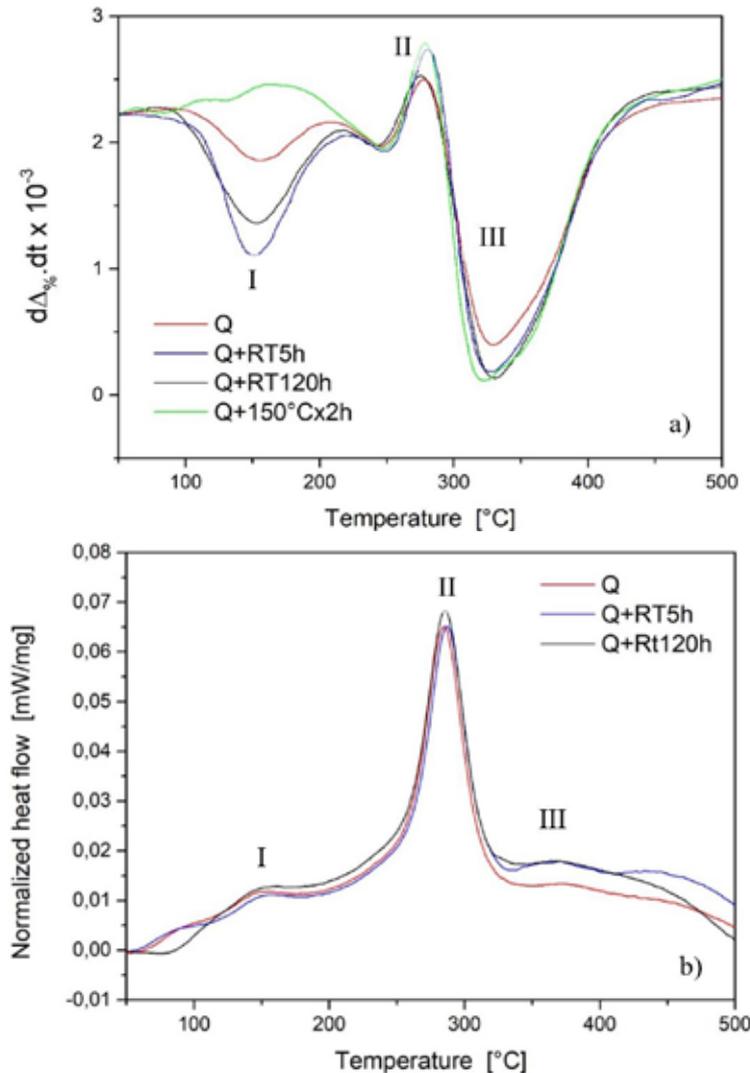


Fig. 5 - Influence of RT soaking on the tempering behavior of tool steel
a) Dilatometric curves and **b)** DSC curves for Q, Q+RT5h and Q+RT120h samples

A first interesting result is the markedly larger contraction due to transition carbides precipitation (peak I in Fig. 5a). This effect becomes less evident after 120h than after 5h. Furthermore, the peak positions of Q+RT5h and Q+RT120h are shifted towards slightly lower temperature compared to Q, suggesting the lower activation required for precipitation. A similar, but less evident effect, can be observed also for the precipitation of cementite (peak III), which becomes more intense after RT ageing.

The most plausible reason for the stronger precipitation of transition carbides is the Carbon redistribution during RT ageing, in particular the enhanced "natural" clustering oc-

curing at RT compared to that occurring during "artificial" clustering during tempering. Clustering at RT is corroborated by previous work showing a decrease of unit cell volume of martensite during RT ageing of Fe-1.13%C for less than 50h [7]. In the same time frame no significant structural change in the austenite occurred. Aging for time longer than 50h further decreases the cell volume, due to a decrease of c lattice parameter, but less than during the early period. The lack of the first DSC shoulder in Q+RT120h is in good agreement with previous findings and confirms that clustering is almost completed after long time aging at RT. On the other hand, the limited enthalpy change associated to transition carbides pre-

Heat treatment

precipitation, makes the effects highlighted by dilatometry less obvious (Fig.5b). The stronger exothermic peak between 300 and 400°C for both Q+RTx samples is in good agreement with the stronger contraction due to cementite precipitation (peak III).

Looking to the peak related to austenite decomposition (peak II), it does not show any appreciable influence of RT stay even if, it seems to be slightly higher in Q+RT5h than in Q. Obviously, this effect is not related to any change in RA content, since no decomposition of this phase is permitted at temperature lower than 200°C [1,12]. It could be directly related to Carbon redistribution at RT or, indirectly, to the effect of this redistribution on transition carbides precipitation. Ongoing investigations carried out by the same authors on a different tool steel (AISI D2), including a more systematic synchrotron X-ray diffraction analysis, seem to confirm the possible occurrence of C partitioning or a stronger stress relaxation of austenite after 5hRT ageing [13]. A preliminary annealing process at 150°C for 2h, leading to the precipitation of transition carbides (see green line in Fig. 5a), shows an expansion due to RA decomposition very similar to Q+RT5h.

Considering the effect of DCT, it is possible to observe that it causes a stronger transition carbide precipitation and a shift toward lower temperature with respect to Q+RTx sam-

ples (Fig.6). Again, a similar conclusion can be drawn also for the precipitation of cementite, confirming that DCT plays the same influence described for sample cryotreated immediately after quenching (Figure 4). So, this effect is brought by the higher fraction of martensite after DCT, i.e., the higher amount of ϵ -carbides, which are available for the cementite precipitation. The latter process involves the participation of the carbon contained in transition carbides and the one contained within martensite, segregated or in solid solution [1,8]. A possible reason for the stronger cementite precipitation is also the stronger Carbon segregation produced by DCT: it has been shown that the soaking in LN can greatly improve the dislocation density responsible for segregation. This thesis is actually under investigation by other techniques (XRD diffraction), that can give direct information about the martensite structure. Independently from RT soaking time, the peak related to austenite decomposition is always present, suggesting that the effectiveness of DCT becomes clearly lower than just after quenching. The expected retained austenite stabilization produced by RT soaking is evident. It follows that the complete decomposition of RA can occur only during tempering. In other words, DCT cannot be used as a panacea to correct the effects of an improper heat treatment practice.

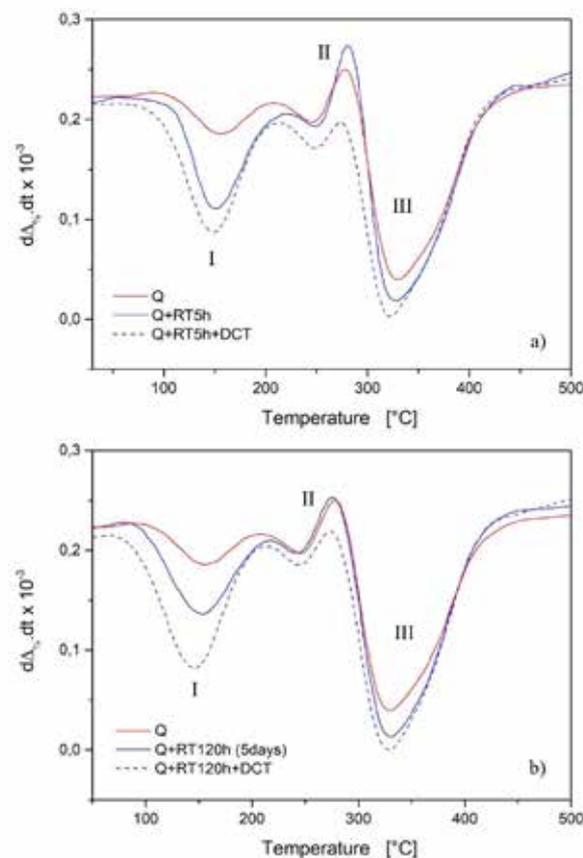


Fig. 6 - Dilatometric curves recorded during isochronal tempering of quenched samples stabilized at RT for **a)** 5 hours and **b)** 120 hours (5days).

CONCLUSIONS

The effect of RT aging on the microstructural transformations during tempering of a 72NiCrMo4-2 low alloyed tool steel has been investigated. A stronger contraction between 70 and 220°C due to transition carbides precipitation is well evident after 5 and 120h aging, suggesting some Carbon redistribution occurring at RT. In present steel, clustering completely occurred during aging for 120h. A stronger contraction due to cementite precipitation is also observed between 220 and 420°C. Retained austenite stabilizes during RT aging: a higher expansion during its decomposition occurs after 5h aging, suggesting two possible phenomena, to be further verified, i.e. a C partitioning or a stronger stress relaxation. DCT for 30min in LN produces the partial transformation of retained austenite. The higher amount of martensite leads

to stronger transition carbides precipitation, as well as to more intense cementite precipitation at higher temperature. The efficacy of DCT is higher when carried out immediately after quenching, as demonstrated by the disappearance of expansion in dilatometric curves. Indeed, after 5 and 120h RT ageing the expansion is still quite large, confirming that the complete transformation of retained austenite can occur only during final tempering.

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