Dilatometric investigations of phase transformations at heating and cooling of hardened, unalloyed, high-carbon steels

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Materials

ABSTRACT

Purpose: The reason for writing this paper was to describe the kinetics of phase transformations during continuous heating from hardened state and subsequent cooling of unalloyed high carbon steel.

Design/methodology/approach: Dilatometric investigations were performed using a DT 1000 dilatometer of a French company Adamel. Samples after quenching and quenching and sub-quenching in liquid nitrogen (-196 °C) were heated up 700 °C at the rate of 0.05 °C/s and subsequent cooled to room temperature at the rate of 0.05 °C/s.

Findings: Regardless of heating the hardened high-carbon steel to 700 °C, a small fraction of the retained austenite remained in its structure, and was changing into fresh martensite only during cooling in the temperature range: 280°C-170°C.

Research limitations/implications: Schematic presentation of the differential curve of tempering of the hardened high-carbon, unalloyed steel illustrating the phase transformations occurring during heating from hardened state.

Practical implications: An observation, that a small fraction of the retained austenite remained in the structure of tempered high-carbon steel, indicates that even unalloyed steel should be tempered two times.

Originality/value: Detailed descriptions of kinetics phase transformations during heating from hardened state of unalloyed high carbon steel.

Keywords: Metallic materials; Tempering; Phase transformations; Dilatometric investigations

1. Introduction

According to the European Standard [1], tempering is a heat treatment applied for ferrous alloys, usually after hardening, which allows to obtain the determined properties. It is based on a single or multiple heating to the determined temperature below Ac_{1s}, holding at that temperature and then cooling with a proper rate. Usually this procedure decreases hardness, however, in some cases hardness can be increased.

Tempering [2] can be:
1) Low (150-250 °C),
2) Medium (250-500 °C),
3) High (500-Ac_{1s} °C),
and structures of tempered steel previously hardened into martensite are:
1) Low-tempered martensite,
2) Medium-tempered martensite,
3) High-tempered martensite.

Tempering of completely or partially martensitic structures at a temperature below 200 °C is called sometimes [1, 2] stress relief tempering – this is tempering performed usually to remove own stresses by aging (redistribution of some part of interstitial elements, mainly carbon, into defects in martensite) and to obtain precipitations of the first, metastable carbides without significant hardness lowering.

So far, at tempering of hardened steel the following phase transformations have been singled out:
1) Carbides precipitation:
   a) transient:

χ-$Fe_{2,5}C$, ε-$Fe_{2,4}C$, η-Fe_2C – nucleate independently, taking carbon directly from martensite, precipitating in hardened steels medium and high-carbon, low-alloy and alloy, at tempering temperatures up to app. 200 °C [3-7]. Along with a gradual increase of tempering temperatures they undergo dissolving, forming then independently nucleating cementite M_3C;

M_3C – nucleates independently [8], precipitating in tempered steels above 200 °C, which in alloy steels - containing in a hardened matrix strongly carbide forming elements such as V, W, Mo, – at temperatures higher than 450 °C undergo dissolving and form independently nucleating carbides of these elements, of the type: MC and M_2C;

M_2C – nucleates independently [9-13], precipitating in tempered alloy steels containing Mo or W in a hardened matrix, at temperatures above 450 °C. At tempering temperatures of app. 700 °C it undergoes transformation by means of the "in situ" nucleation mechanism into carbides of the type: M_6C and MC;

M_7C_3 – nucleates in steels containing Cr by the „in situ" mechanism [9], at temperatures above 450 °C when Cr concentration in cementite M_3C achieves app. 18 %, and then at the Cr content app. 50 % undergoes transformation, also by the „in situ" mechanism, into carbides $M_{23}C_6$.
   b) stable:

M_3C – nucleates independently [8], precipitating in tempered ordinary and low alloy steels, in a range: 200 °C – 425 °C along with dissolving of metastable carbides χ-$Fe_{2,5}C$, ε-$Fe_{2,4}C$, η-Fe_2C;

M_7C_3 – nucleates in steels containing Cr by the „in situ" mechanism [9], at temperatures above 450 °C, when the Cr concentration in cementite M_3C achieves app. 18 %, but the concentration of this element in a matrix of tempered steel is insufficient to form carbides $M_{23}C_6$, more reach in Cr;

$M_{23}C_6$ – nucleates by the „in situ" mechanism [9] via the Cr cumulation above 50% in carbides of the type M_7C_3.;

MC – nucleates independently [11, 14-19], precipitating in tempered alloy steels containing V or Nb in hardened matrix, at temperatures above 450°C, as metastable carbides of the type M_3C dissolve.

2) Transformation of the retained austenite:
   a) at heating – in lower bainite [19, 20] generally within the precipitation temperature range of cementite M_3C, in middle-carbon and high-carbon steels, unalloyed and alloyed steels;
   b) at cooling after tempering – in martensite [21, 22], in high-alloyed steels.
3) Recrystalization of a hardened (defected) matrix – at temperatures usually above 650 °C [23].

2. Analysis of dilatograms of tempering from a hardened state on martensite

A part of listed above transformations can be easily indicated in dilatograms of tempering high-carbon steels. In Fig. 1a there is a dilatogram of tempering in the system: $\Delta L = f(T, °C)$ of steel C110 previously hardened into martensite from a homogenous austenite (T_A = 900 °C) – marked by H. For a comparison a heating dilatogram of the same steel, but in unhardened state (soft annealing) is also presented in this Figure – marked by N.

It is easy to notice (Fig. 1a), that when the unhardened sample is extended with a temperature (N), none dilatation effects are seen, while the extension of the hardened sample (H) is accompanied by two negative and one positive dilatation effect. The first negative effect (which range is marked by I), recorded from nearly a room temperature up to 200 °C, is the sample shrinkage, related to the precipitation of independently nucleating transient carbides: χ-$Fe_{2,5}C$ of a monoclinic lattice, ε-$Fe_{2,4}C$ of a hexagonal lattice and η-Fe_2C of a rhombic lattice (mentioned in point 1a), however mainly carbide ε.

The second negative dilatation effect (marked in Fig. 1 by II), is the sample shrinkage related to the precipitation of independently nucleating cementite M_3C. It starts at a temperature of 200 °C and continues up to a temperature of app. 425 °C. However, at the very beginning of this temperature range (marked as IIA) the positive dilatation effect, related to the transformation of the retained austenite, occurs. Thus, within the temperature range IIA two effects are summing: the shrinkage caused by the precipitation of independently nucleated cementite Fe_3C and the volume increase caused by the transformation of the retained austenite into lower bainite. At a large fraction of the retained austenite in microstructure of hardened steel (at high carbon content in austenite of hardened steel), the effect related to its transformation can be higher than the shrinkage effect caused by the cementite precipitation. Therefore in Fig. 1b illustrating changes in the length increase difference of the hardened (H) and unhardened sample (N): $(\Delta L_H - \Delta L_N) = f(T, °C)$ within the temperature range of the retained austenite transformation (IIA) hampering of the difference increase between elongations of both samples is noticed and in the curve illustrating this difference a hump occurs. Cementite M_3C precipitating above 200 °C acc. takes carbon mainly from dissolving transient carbides and only in small part from the martensitic matrix. It is worth to notice, that after the end of the cementite precipitation process at 425 °C, the difference of length increases $\Delta L_H - L_N$, is still rising (becomes more negative), the most probably due to the coagulation of the cementite particles precipitating from martensite in the sample (H).
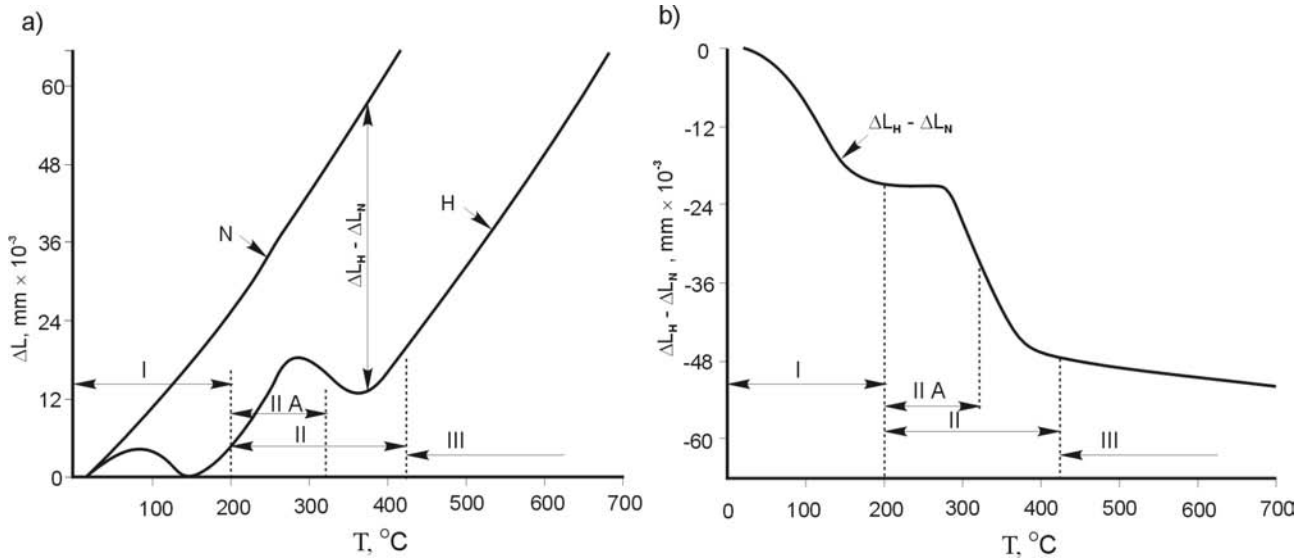
Fig. 1. a) Elongation changes ΔL of samples of initial lengths of 12 mm made of steel C110 hardened on martensite (line H) from a homogenous austenite range (900 °C) and unhardened (line N) - with a heating temperature, b) Change of the length increase difference: $\Delta L_H - \Delta L_N$ of both samples - with a heating temperature

The heating dilatogram in the system $\Delta L/L_0 = f(T, °C)$ of the steel sample C110 hardened from the homogeneous austenite range (this is the basic dilatogram for calculation the dependence $\Delta L = f(T °C)$ marked H in Fig.1a) together with the corresponding differential curve: $d(\Delta L/L_0)/dT = f(T, °C)$ is shown in Fig. 2.
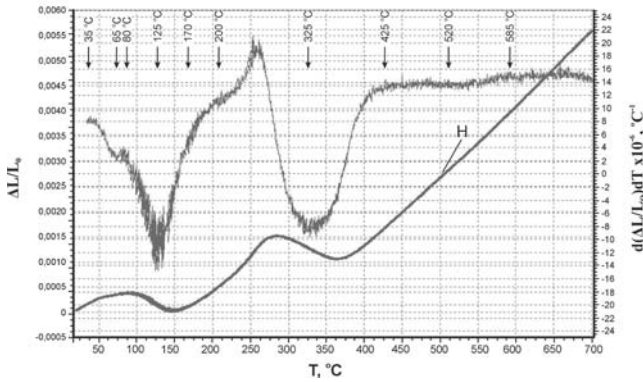

Fig. 2. Heating dilatogram with a rate of 0.05 °C/s of the hardened sample, not subquenched of a length 12 mm of steel C110, illustrating the relative change of the sample length increase $(\Delta L/L_0)$ as a function of the heating temperature (T, °C) and the differential curve: $d(\Delta L/L_0)/dT$, corresponding to these changes

This differential curve revealed several details of transitions occurring at tempering, which were not well visible in the main dilatogram. First of all, already at 35 °C the thermal extension of the sample started to be hampered by the shrinkage related to the precipitation process, or more precisely to martensite aging. However, this stage finished at 65 °C. Starting from 65 °C the shrinkage process stopped and the visible positive dilatation effect

dominated, but only to 80 °C. Above this temperature, again the shrinkage started to dominate. This shrinkage was the most probably related to the advanced precipitation of transient carbides, mainly carbide ε, from martensite. This precipitation achieved the highest intensity (the smallest differential value) at a temperature of 125 °C. Then the precipitation became weaker, probably because of the carbon content decrease in the surrounding matrix (martensite) (compare data in Fig. 3) due to an increasing temperature, which started to favour the precipitation of carbides Fe_3C (M_3C) stable in unalloyed steels.
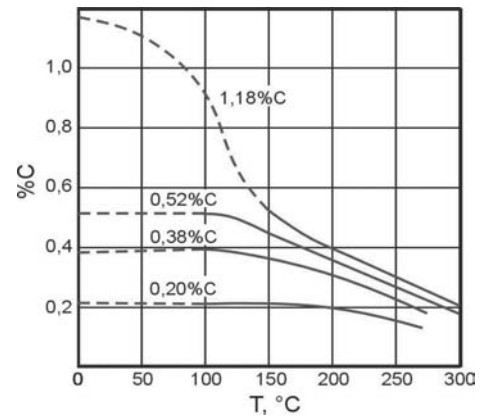

Fig. 3. Influence of the tempering Temperature (T_T) on the carbon content (%C) in martensite of unalloyed steels, acc. S. Prowans [24]

A temperature of 200 °C (Fig. 2) can be indicated as the one at which the precipitation of transient carbides stopped, since at this temperature the break-down of the differential value increase was noticed. Above 200 °C the differential and − first of all − the

main dilatogram the most probably would have indicated the shrinkage related to the cementite M_3C precipitation, however above 200 °C the transformation of the retained austenite into lower bainite, called sometimes (due to similar morphological features) tempered martensite, had occurred. Such transformation is accompanied by the strong positive dilatation effect. This stage of the transformation of the retained austenite continues up to a temperature of app. 325 °C, at which the positive dilatation effect decays for the shrinkage – lasting all the time (from app. 200 °C) – related to the cementite (M_3C) precipitation.
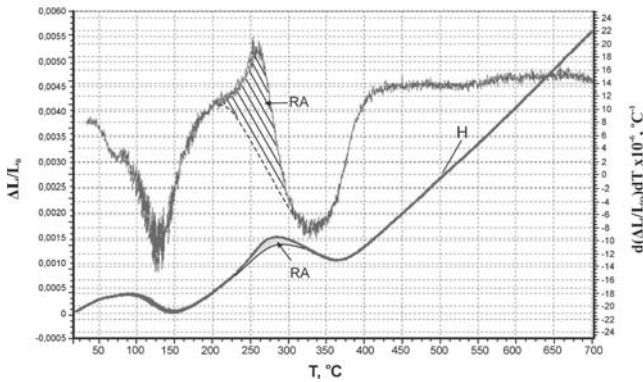

Fig. 4. Dilatogram of heating with a rate of 0.05 °C/s together with the differential curve for the hardened sample, not subquenched, of a length of 12 mm of steel C110 (see Fig. 2) with shaded fields of the retained austenite transformations
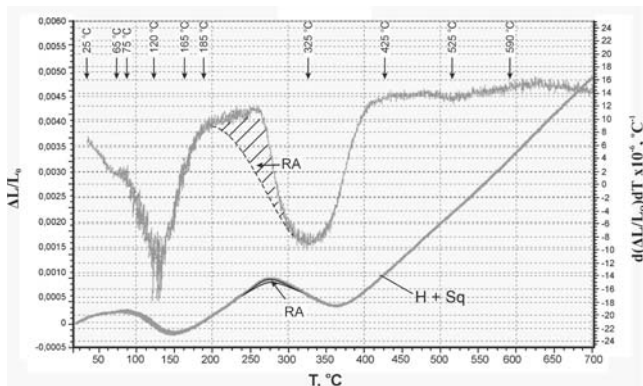

Fig. 5. Dilatogram of heating with a rate of 0.05 °C/s of the hardened steel C110 sample of a length of 12 mm additionally subquenched in liquid nitrogen (at -196 °C) for 1 hour, illustrating the relative change of the sample length increase ($\Delta L/L_0$) as a function of the heating temperature (T, °C) and the corresponding differential curve $d(\Delta L/L_0)/dT$

If the retained austenite had not been present in this steel structure, the course of the differential curve in the range 200 °C-325 °C would have been - in approximation – the same as the one marked by the dashed line in Fig. 4. Shaded fields in this Figure (both in the main dilatogram and in the differential graph) reflect effects caused by the retained austenite transformation (RA).

Confirmation of this statement can be the heating dilatogram of the sample hardened in the same way (from 900 °C) and additionally subquenched in liquid nitrogen (at -196 °C) for 1 hour (Fig. 5). As it is seen, the positive dilatation effects from the retained austenite transformation (RA – fields also shaded) are evidently smaller than in not subquenched sample (see Fig. 4), both in the main dilatogram and in the differential curve.

According to the proposed in this study interpretation of dilatograms of tempering unalloyed high-carbon steel, the precipitation of cementite (M_3C) starts directly after the precipitation of transient carbides χ-$Fe_{2,5}C$, ε-$Fe_{2,4}C$, η-Fe_2C, finishes, which means that in the not subquenched sample at 200 °C (Fig. 2) while in the subquenched one at 185 °C (Fig. 5) and lasts up to 425 °C. Above this temperature only the coagulation of the precipitated cementite particles should occur. However, in reality, one more small increase in volume can be seen, but it is noticeable only in differential curves, for not subquenched sample (Fig. 2) in the range: 520 °C-585 °C while for the subquenched one (Fig. 5) in the range: 525 °C-590 °C. If this is an effect related to the retained austenite transformation, such austenite should be called the "persistent austenite". It is worth to mention, that during this tempering (heating with a rate of 0.05 °C/s) the transformation of the "persistent austenite" (the most probably into fine pearlite) occurs in the temperature range: 500 °C-600 °C, which means precisely in the range of the temper brittleness of the 2nd kind occurrence. Thus, it should be checked whether the "persistent austenite" transformation contributes to the formation of this brittleness. In such case, the theory of the diffusion entering into the grain borders of harmful elements such as P, As, Sb, Sn etc., during slow cooling after tempering, which explains this effect (also in unalloyed steels) would be limited. However, if the observed gain in volume of the tempered sample in the range: 500 °C-600 °C is related to the austenite transformation, the assigned to it – in this study – name of the "persistent austenite" is the most proper one, since it is preserved at tempering up to: 500 °C-600 °C. Taking the dilatation effect value as the base for the estimation (in differential curves in Figs. 2 and 5), its fraction in the steel structure does not depend on the subquenching degree of the hardened sample. However, its complete liquidation during the first tempering, not necessary by the transformation into fine pearlite, but into arbitrary other components at cooling after the first tempering, should either liquidate or limit the occurrence of the temper brittleness of the 2nd type – after the successive heating (into the range: 500 °C-600 °C) of the tempered sample. Thus, not denying the current theories of temper brittleness of the 2nd type, we are pointing out to one more factor, which can cause this brittleness or at least contribute to its value − and this is the "persistent austenite".

Both tempering dilatograms (for not subquenched and for subquenched samples) and corresponding differential curves are drawn, in the same scale, in Fig. 6. It is seen from the comparison that the intensity of the transient carbides precipitation in the sample subquenched is higher but only during the initial phase, it means up to a temperature of app. 125 °C, when the main dilatometric curve achieves the point of inflection and the differential obtains its minimum. It is displayed by smaller differential values for the sample subquenched in the range to app. 125 °C. The intensity of the transient carbides precipitation in the range: 125 °C-200 °C is in both samples nearly the same,

since the differential curves coincide and the main dilatometric curves are parallel to each other. However, it is worth noticing that the higher intensity of the transient carbides precipitation in the subquenched sample (in the range to app. 125 °C) caused such sample shortening that its length in the temperature range: 125 °C-185 °C (Figs. 5 and 6) is smaller than directly after hardening. Both samples, not subquenched and hardened, obtain − in the range of the transient carbides precipitation − the length minimum at app. 150 °C (Fig. 6). The difference in the length of not subquenched and subquenched samples, the most probably, would have been remained also at higher tempering temperatures if not the transformation of a larger amount of the retained austenite into lower bainite in the not subquenched sample in the range: 200 °C-325 °C. The dilatometric curves of both samples are parallel from a temperature of 325 °C (Fig. 6) and their differential curves coincide. It is worth to mention that the transformation of a larger volume of the retained austenite in not subquenched sample increased the length differences of both samples (Fig. 6), which were of the same length 12.0 mm in the moment of starting heating (at app. 20 °C).
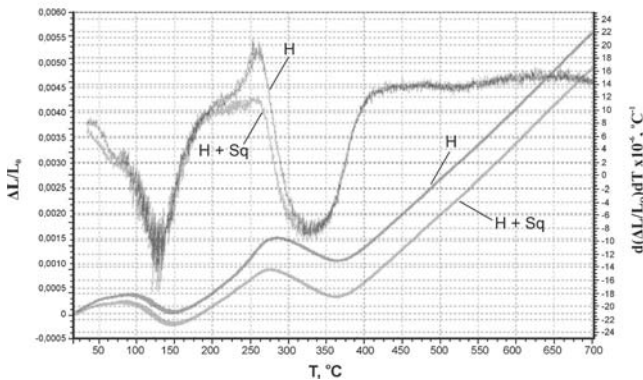

Fig. 6. Dilatograms of heating with a rate of 0.05 °C/s of the hardened but not subquenched samples and the hardened and additionally subquenched samples in liquid nitrogen (at -196 °C) for 1 hour. Samples of steel C110 of initial length 12 mm, illustrate the relative length increase ($\Delta L/L_0$) as a function of the heating temperature (T, °C). The differential curves corresponding to these changes $d(\Delta L/L_0)/dT$ are drawn in the same scale

Looking at the recorded dilatograms and their corresponding differential curves (Figs. 2 and 5) it can be noticed, that in the transient carbides precipitation range two characteristic refractions of the differential occur (repeating also in other heating dilatograms of this steel). For the not subquenched sample they occur at: 65 °C-80 °C (increased differential value) and at app. 170 °C (decreased differential value) – Fig. 2, while for the subquenched sample at: 65 °C-75 °C (increased differential value) and at app. 165 °C (decreased differential value).

Distinct and repeating elongation of the sample in ranges: 65 °C-80 °C and 65 °C-75 °C could be related to the variation in the precipitation character. Up to 65 °C it would be the classic aging, i.e. displacing of carbon atoms from martensite to structural defects, and above 80 °C (75 °C in the subquenched

sample) the transient carbides precipitation. However, it is not known why at a temperature of app. 170 °C (in not subquenched sample) and app. 165 °C (in the subquenched sample) differentials (i.e. also the sample length) slightly decrease. The significant differential increase in ranges: 65 °C-80 °C (Fig. 2) and 65 °C-75 °C (Fig. 5) remains still without explanation.

The statement that in the range: 65 °C-170 °C – in not subquenched sample (Fig. 2) and in the range: 65 °C-165 °C – in the subquenched sample (Fig. 5) the transformation of the first part of the "least stable" retained austenite occurs could have been a reliable explanation of these increases and decreases of the differential value. Decreasing compressive stresses (due to carbon precipitating from martensite) could be the factors generating this transformation. That means, that in the temperature range: 65 °C-170 °C – in not subquenched sample and: 65 °C-165 °C – in the subquenched sample, apart from the transient carbides precipitation, the transformation of the "least stable" retained austenite takes place. If, on the typical tempering dilatogram (expressed by means of the differential curve 1-2-3-4-5-6-7-8-9-10 shown in Fig. 7) the positive effect from the transformation of the "least stable" retained austenite (presented by line 2-11-4) is deposited – in the transient carbides precipitation range – then the characteristic refractions will appear on the basic differential curve (in ranges 2-12 and 14-4), noticeable in actual dilatograms (Figs. 2 and 5).

The positive dilatation effect generated by the transformation of the "least stable" retained austenite – in the transient carbides precipitation range – explains well the refractions in the diffraction curve in this range. However, such effect should lower the shrinkage effect caused by the transient carbides precipitation. Then the differential curve should cover the line 2-12-13-14-4 (see scheme in Fig. 7). Whereas, above a temperature of 90 °C up to 160 °C – in not subquenched sample and from 85 °C to 155 °C – in the subquenched sample (Figs. 2 and 5) a very intensive shrinkage appears. These temperatures, in the scheme shown in Fig. 7, are within the range of points: 15-18-17. It is unlikely, that such intensive shrinkage is caused by the transient carbides precipitation only. However, it can be the shrinkage generated by the "new austenite" formation, expressed by the line 15-16-17, which together with the resultant shrinkage (from the transient carbides precipitation and positive effect of the "least stable" retained austenite transformation − line 2-12-13-14-4) generates the summary strong shrinkage effect of the course: 15-18-17.

The "new austenite" could be formed due to dissolving of unstable transient carbides and carbon redistribution into iron, but not so uniform as it was in martensite. The privileged place of the new position of the repeated carbon atoms freeing is, first of all, the nearest area of dissolving transient carbides and – of course – structural defects existing there. How large pressure (compressive stresses) in the iron structure can cause such repeated transfer of carbon atoms into the matrix (in between iron atoms) can be only assumed, e.g. on the grounds of a large fraction of the retained austenite in this steel directly after hardening, when carbon atoms were situated uniformly. The introduction of the same carbon atoms in between iron atoms in an uneven way (redistribution of carbon atoms), must locally cause specially large stresses, so large, that they can be able to cause a reverse transformation: $Fe_\alpha \rightarrow Fe_\gamma$, which must be accompanied by the negative dilatation effect.
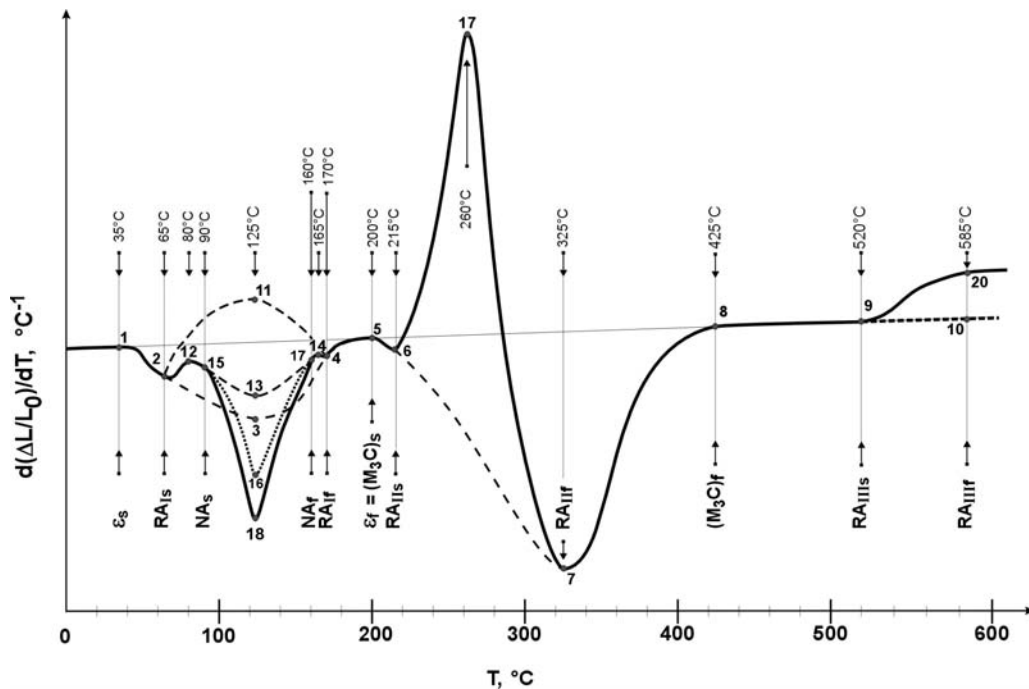
Fig. 7. Schematic presentation of the differential curve of tempering of the hardened high-carbon, unalloyed steel illustrating the phase transformations occurring during heating. Markings:

ε_s – start of carbide ε precipitations (transient carbides),

RA_{Is} – start of the "least stable" retained austenite transformation,

NA_s – beginning of the "new" retained austenite formation,

NA_f – finish of the "new" retained austenite formation,

RA_{If} – finish of the "least stable" transformation,

ε_f – finish of the carbide ε precipitations (transient carbides),

$(M_3C)_s$ – start of the cementite precipitation,

RA_{IIs} – start of the "main" retained austenite transformation,

RA_{IIf} – finish of the "main" retained austenite transformation,

$(M_3C)_f$ – finish of the cementite precipitation,

RA_{IIIs} – start of the "persistent" retained austenite transformation,

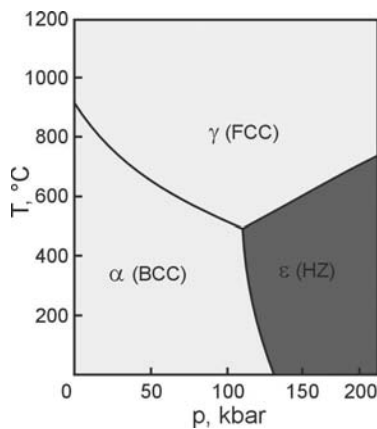RA_{IIIf} – finish of the "persistent" retained austenite transformation

Fig. 8. Influence of pressure (p) on the temperature ranges of Fe_α, Fe_γ and Fe_ε existence, acc. to F.P. Bundy [25]

The transformation $Fe_\alpha \rightarrow Fe_\gamma$ (temperature Ac_3) is possible at the determined conditions of temperature and pressure. According to F.P. Bundy [25] (Fig. 8), along with the pressure increases the temperature Ac_3 of iron can be decreased from 912 °C even to app. 480 °C, (at pressure being equal app.110 kbars (1 kbar = 981 at).

However, above 130 kbars the transformation: $Fe_\alpha \rightarrow Fe_\varepsilon$ is possible (of a hexagonal lattice) even at an ambient temperature. This is not difficult to understand seeing (Fig. 9) how small shifting require Fe_α atoms in the plane (110) to assume the highest density configuration typical for Fe_γ in the plane (111), or the highest density configuration typical for Fe_ε in the plane (1000).
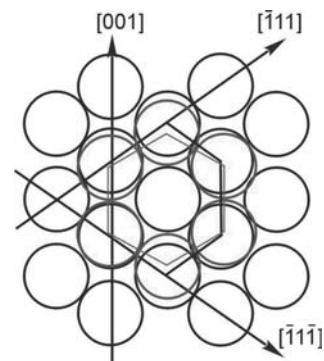

Fig. 9. Arrangement of atoms in the plane (110) of BCC structure, acc. T. Malkiewicz [9]

The recorded basic dilatograms indicate the transformation complexity (superpositioning) in the range of low tempering temperatures of the investigated unalloyed, high-carbon steel. It is seen quite distinctly (see Figs. 2 and 5), that in the range: 80 °C to 170 °C – for not subquenched sample and in the range: 75 °C to 165 °C – for the hardened sample, dilatometric curves are visibly "smeared over", which indicates a simultaneous occurrence of transformations having the opposing dilatation effects. The positive effect is the most probably related to the transformation of the "least stable" retained austenite. Whereas the negative effects can be attributed to the transient carbides precipitation and to the "new austenite" formation due to the carbon redistribution in iron.

The indicated above redistribution of carbon in the tempered steel structure due to dissolution of metastable transient carbides the most probably caused the "new austenite" formation, regardless of the main retained austenite existing already after hardening. The "least stable" of the existing austenite part, could be even undergoing a gradual transformation when and − in those places − where transient carbides were precipitating. However, in those places where transient carbides started dissolution, from the moment of achieving there the sufficiently high pressures (compressive stresses because of the local, strong iron enrichment with carbon), the reverse transformation is possible: $\alpha \rightarrow \gamma$ or $\alpha \rightarrow \varepsilon$, regardless of a low temperature. This is not an interfacial reaction but the reaction within a single phase.

The transformation of $\alpha \rightarrow \varepsilon$, more probable on the grounds of data provided by F.P. Bundy [25] (Fig. 8) because of a relatively low temperature of this transformation, seems less real during tempering although, as it is known, Fe atoms in the transient carbides precipitation range are forming the hexagonal system. However, this system is attributed to carbides ε ($Fe_{2,4}C$), which being interstitial phases have Fe atoms in the hexagonal system. The transformation of $\alpha \rightarrow \gamma$ in the range of low tempering temperatures (dissolution of transient carbides) was already several times identified, among others in papers [26], both by means of the light microscope (Fig. 10) and in X-ray examinations (Fig. 11).

However, up to now, the authors as well as the reviewers doubted in this experiment suggesting, that it might not be the "new austenite" formed as a result of the transient carbides dissolution, but the main austenite which remained in the microstructure during the hardening procedure, and only due to a higher tempering temperature (200 °C) underwent a stronger stabilization than the one tempered at 100 °C (Figs. 10 and 11), which managed to transform partially into martensite − on the sample surface − during the metallographic micro-section preparation. However, the results of investigations of crack resistance [27] of steel 0.70 %C, 2.15 %Mn, 0.54 %Cr, 0.44 %Mo performed by the K_{Ic} method (Fig. 12) and by the impact method KCU2 (Fig. 13) originate from the whole sample volume and indicate the maximum crack resistance exactly after such tempering (at 210 °C) when the retained austenite fraction – found by the X-ray method – was the largest.
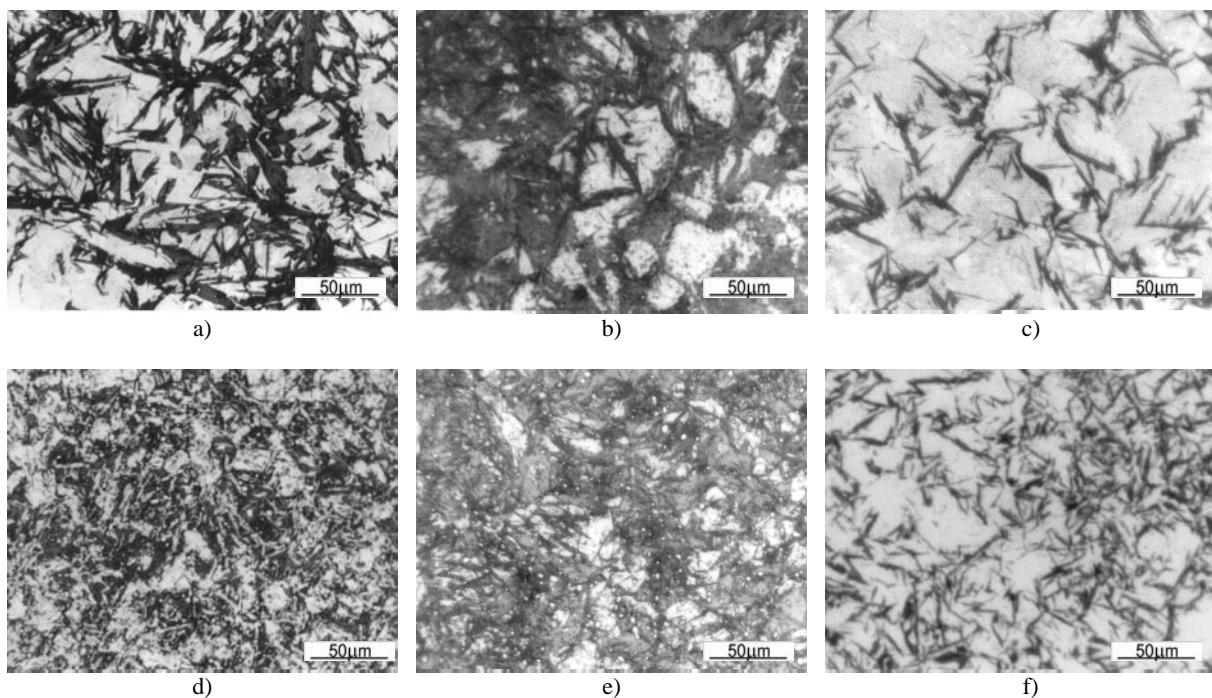

Fig. 10. Photographs of microstructures of steel samples: No 7 (1.22 %C, 1.93 %Mn, 1.52 %Cr, 0.36 %Mo) and No 18 (1.09 %C, 1.47 %Mn, 1.91 %Cr, 0.43 %Mo) hardened from 960 °C and after tempering at 100 °C and 200 °C. Magnification 600x, etched by 2 % nital, acc to [26]: a) No 7, hardened; b) No 7, $T_T = 100$ °C; c) No 7, $T_T = 200$ °C; d) No 18, hardened; e) No 18, $T_T = 100$ °C; f) No 18, $T_T = 200$ °C
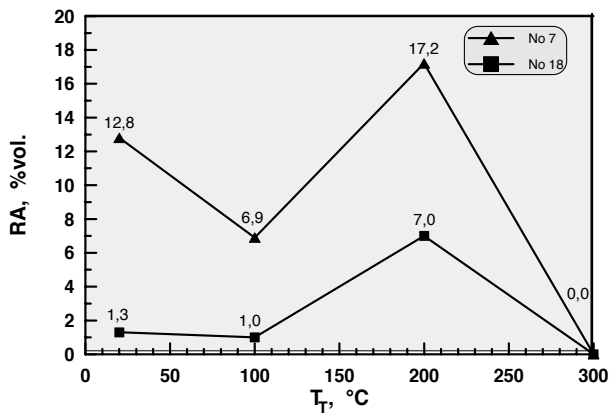
Fig. 11. Influence of the tempering temperature T_T (for 2 h) on the retained austenite volume fraction (RA) in hardened from 900 °C and later on subquenched at -196 °C (for 1 h) steel samples: No 7 (1.22 %C, 1.93 %Mn, 1.52 %Cr, 0.36 %Mo) and No 18 (1.09 %C, 1.47 %Mn, 1.91 %Cr, 0.43 %Mo) – estimated by the X-ray method, acc. to [26]
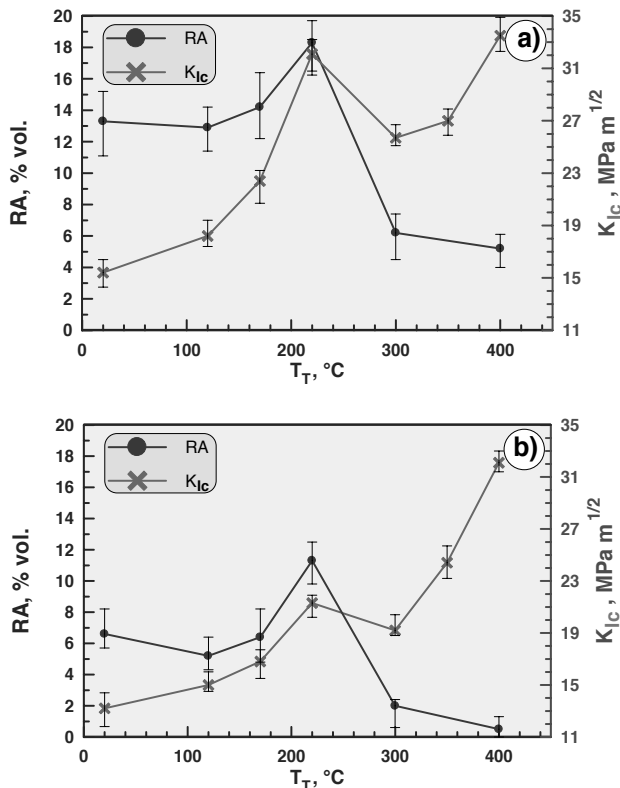

Fig. 12. Influence of a tempering temperature on the stress intensity factor (K_{Ic}) and volume fraction of the retained austenite (% vol.) in hardened from 820 °C steel 0.70 %C, 2.15 %Mn, 0.54 %Cr, 0.44 %Mo in state: a) without subquenching; b) after subquenching 0.70 %C, 2.15 %Mn, 0.54 %Cr, 0.44 %Mo at -196 °C, acc. to [27]
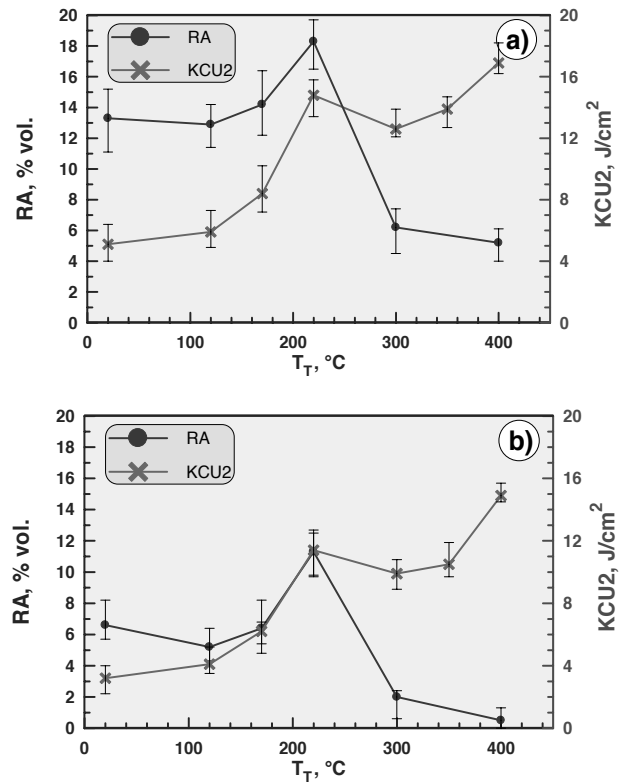

Fig. 13. Influence of a tempering temperature on the impact strength (KCU2) and volume fraction of the retained austenite (% vol.) in hardened from 820 °C steel 0.70 %C, 2.15 %Mn, 0.54 %Cr, 0.44 %Mo; in state: a) without subquenching; b) after subquenching at -196 °C, acc. to [27]

Knowing, on the grounds of papers [19, 20], that each volume percent of the retained austenite in tool steels increases their crack resistance (K_{Ic}) by 5 % and in case of steels − after hardening and tempering of the retained austenite system in a form of a film in between martensite laths − even much more [28-30]. The problem of this phase in hardened and tempered steels should be treated as the investigation priority. Especially presently, when on the grounds of the performed investigations [22], it is possible to stabilise this retained austenite so effectively that it remains as a stable phase, at least to the elasticity level limit.

The recorded tempering dilatograms indicate that the retained austenite problem in the investigated high-carbon C110 steel does not end – in spite of the fact that it is unalloyed steel – when it is heated to 700 °C after being hardened. It turns out that during cooling after such high tempering (Fig. 14) the retained austenite transformation into fresh martensite occurs still in the range: 280 °C to 170 °C. It is characteristic that this transformation occurs in the same temperature range in samples without and with subquenching. This austenite is really the retained austenite since the successive heating and cooling does not show any special dilatation effects neither in the differential curves nor in the main dilatograms. However a fact that, even after so high tempering (at 700 °C), a certain small fraction of the retained austenite remains in the unalloyed steel structure, which undergoes transformation

into fresh martensite only during cooling, indicates that every steel grade, even unalloyed, should be at least two times tempered after hardening.
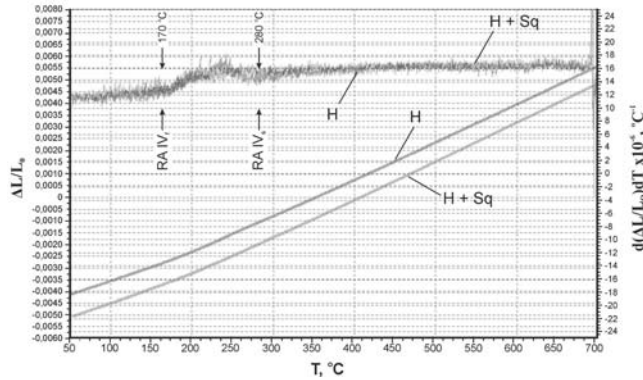

Fig. 14. Dilatograms of cooling with a rate of 0.05 °C/s of C110 steel samples previously hardened (H) and hardened and later subquenched (H+Sq), heated to 700 °C (as in Fig. 2 and 5) illustrating relative changes of shortening samples ($\Delta L/L_0$) as a function of temperature (T, °C) and the corresponding differential curves d($\Delta L/L_0$)/dT
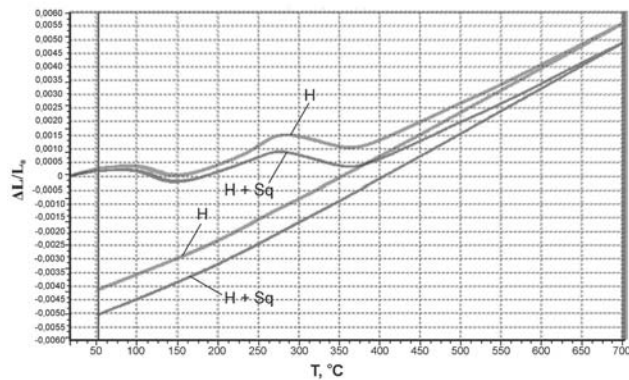

Fig. 15. Dilatograms of heating with a rate: 0.05 °C/s up to 700 °C and then cooling with the same rate to 55 °C of steel C110 samples previously hardened (H) and hardened and subquenched (H+Sq), illustrating relative changes of sample lengths ($\Delta L/L_0$) as a function of temperature (T, °C)

The set of the recorded main dilatograms is presented in Fig. 15. These dilatograms illustrate changes in not subquenched and in subquenched samples of the same initial length (12 mm) during their heating to 700 °C and then cooling to a temperature of app. 55 °C. As can be seen, the sample which was not subquenched remains longer than the one which was subquenched, both after heating to 700 °C and after cooling to 55 °C. This is due to a: smaller shrinkage within the initial aging (to app. 80 °C), smaller shrinkage in the range of the intermediate carbides precipitation from martensite, smaller shrinkage during the "new austenite" formation when these carbides are dissolving, large elongation because of the transformation of a larger amount of the main austenite (existing after hardening) and the "new

austenite". In addition, the not subquenched sample shrinks slightly slower (in this temperature range), which is indicated by the negligibly smaller differential value (Fig. 14).

3. Conclusions

On the grounds of the detailed analysis of dilatograms of heating the high-carbon, unalloyed steel C110 from the hardened state and the differential curves of these dilatograms digitally recorded in the dilatometer DT 1000 of the French Company Adamel, several observations were performed.

1) The aging process in martensite of the hardened steel, being a near-range diffusion of interstitial atoms to structure defects, starts – the most probably – already at an ambient temperature.

2) The transient carbides precipitation range, related to the evident shrinkage of the investigated sample, is contained within the temperatures range conventionally called ε_s – ε_f. In case of the investigated steel, it is the range: 35 °C-200 °C.

3) The aging process followed by the precipitation of transient carbides, causing a decrease of compressive stresses, enable the gradual transformation of the "least stable" retained austenite, it means that part for which the mechanical stability was dominating. The positive dilatation effect related to this transformation causes characteristic refractions on the differential curve, on the basis of which it is possible to indicate that this (first) part of the retained austenite undergoes the transformation in the range: RA_{Is} – RA_{If}, i.e. 65 °C-170 °C.

4) An increasing tempering temperature in the range: 35 °C-200 °C causes the precipitation of the subsequent transient carbides, a part of which (the most probably of those previously precipitated) looses the stability and dissolves. Carbon redistribution into the matrix due to strong local compressive stresses, causes probably an inverse transformation: $\alpha \rightarrow \gamma$, and the formation of a certain amount of the "new" austenite. The shrinkage accompanying this transformation is recorded on the differential curve by a distinct decrease of its value in the range NA_s-NA_f. This occurs, in the case of the performed investigations, in the range: 90 °C-160 °C. Investigation performed previously, also for high-carbon steels, indicate that a volume fraction of the "new" austenite is larger than the "least stable", which undergoes the transformation due to decreasing compressive stresses.

5) A temperature of the finish of the transient carbides precipitation in the investigated high-carbon steel ε_f is – in approximation – equal the temperature of the start of the cementite precipitation $(M_3C)_s$: app. 200 °C. This cementite precipitation, which in case of this steel is the stable carbide, lasts up to a temperature $(M_3C)_f$ – app. 425 °C. At higher tempering temperatures only its coagulation occurs.

6) The transformation of the "main" part of the retained austenite, the most probably chemically stabilised by atoms of interstitial elements (mainly carbon) takes place within the cementite precipitation range, between RA_{IIs} and RA_{IIf}, temperatures, i.e. between 215 °C and 325 °C.

7) An occurrence of a small fraction of the "persistent" austenite, which transforms itself during heating (probably by means of the diffusive transformation mechanism) only in the range:

520 °C-585 °C, was found in the investigated steel. A chemical stabilization of this part of the retained austenite could have been done by substitutive elements, present in small amounts in unalloyed steel. The transformation range during heating of this (third) part of the retained austenite, called "persistent" is marked by symbols RA_{IIIs} – RA_{IIIf}. This transformation can be related to an occurrence of the so called temper brittleness 2nd type.

8) Regardless of heating the hardened high-carbon steel to 700 °C, a small fraction of the retained austenite remained in its structure, and was changing into fresh martensite only during cooling in the temperature range: 280°C-170°C. The transformation range of this (fourth) part of the retained austenite is marked as RA_{IVs} – RA_{IVf}. This observation indicates that even unalloyed steel should be tempered two times.

9) The recorded main dilatograms confirmed that samples of the same initial length, however containing, due to subquenching, a smaller volume fraction of the retained austenite, will be shorter after tempering.

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