



Irreversible temper embrittlement

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Received 15.06.2013; published in revised form 01.08.2013

ABSTRACT

Purpose: The new approach to the phenomenon of irreversible temper embrittlement was presented in hereby paper.

Design/methodology/approach: Proposed in hereby paper, thesis trying to explain the undesirable known for a long time effect is based mainly on the ground of the authors research experience on the investigating of the fracture toughness as well as phase transformations during tempering.

Findings: The carbon atoms redistribution to the grain boundaries and boundaries of the cellular structure in the martensitic matrix, during dissolving of the metastable carbides, mainly ϵ carbide, was indicated as a main reason of the irreversible temper embrittlement.

Research limitations/implications: Existing, old theories on irreversible temper brittleness such as preferential precipitations from martensite along grain boundaries, chemical and mechanical destabilization of the retained austenite, segregation of admixtures to grain boundaries etc. can be easily invalidated, using modern transmission and scanning electron microscopy.

Originality/value: It was pointed out that the carbon atoms arranged in a privileged places along the grain boundaries and boundaries of the cellular structure, have incomparably stronger influence spread to temper embrittlement rather than existing in thousandths of a percent impurity atoms. The retained austenite (if it exists in the quenched matrix) increases fracture toughness, but it is only an accompanying effect, without any influence on intergranular (and rather intercellular) character of fractures characteristic for this type of brittleness.

Keywords: Fracture mechanics; Temper embrittlement; Phase transformations

Reference to this paper should be given in the following way:

J. Pacyna, A. Kokosza, R. Dziurka, Irreversible temper embrittlement, Archives of Materials Science and Engineering 62/2 (2013) 67-72.

PROPERTIES

1. Introduction

Irreversible temper embrittlement called sometimes blue embrittlement - due to a blue colour of oxides formed on a fresh steel crack surface - occurs after tempering at a temperature of app. 300°C. Therefore it is sometimes also called 'embrittlement 300'. It is absolutely related to phase transformations occurring in a quenched steel matrix at tempering temperatures close to 300°C.

After tempering at temperature of 300°C (see data on Continuous Heating Transformations - CHT diagrams, in Figs. 1, 2, 3), in a majority of quenched steels precipitation of cementite, M_3C , occurs, which precipitated independently [1,2]. In medium-carbon and high-carbon steels a cementite precipitation is in general preceded by a precipitation of ϵ carbide of a formula close to $Fe_{2,4}C$. Metastable ϵ carbide above 200°C are gradually dissolving, supplying carbon atoms for building new, more stable M_3C carbides.

2. Irreversible temper embrittlement in low-carbon steel

Dissolution of ϵ carbides in low-carbon steels causes a new distribution of carbon atoms in a matrix compared with a quenched state. In quenched state, the carbon atoms were distributed approximately at a uniform way and their average concentration was equal to a carbon concentration in a austenite to the quenching.

Released carbon atoms, during dissolution of ϵ carbide, are migrating towards growing nuclei of more stable cementite. Because carbon atoms are relocating themselves by easy diffusion paths (among others by grain boundaries, and by boundaries of cell structures formed already at 300°C), an intensive redistribution of carbon occurs in the structure of tempered steel. This carbon atoms migration towards growing cementite particles continues, as it was several times shown in diagrams of the kinetics of phase transformation CHT - (see Figs. 1, 2, 3), up to a temperature of app. 500°C. If this migration is stopped, by ending of the tempering process at e.g. 300°C, then easy diffusion paths filled ('decorated') with carbon atoms become the ways of easy cracking. This means, that from the beginning of dissolution

of ϵ carbides (app. 200°C) the fracture toughness of the tempered steel should be decreasing and fractures should become intergranular. This is the beginning of the effect of the irreversible temper embrittlement of steel. Its highest intensity occurs at app. 300°C and the fracture toughness attains a minimum.

From the several investigations on this effect point of view, we know that fractures are of intergranular character, moreover these are not only fractures along grain boundaries of a prior austenite but, as it was shown in paper [5], an easy cracking path occurs also along subgrains (cells) boundaries. This is indicated by measurements of a mean fracture path, which is several times smaller than a mean chord of the prior austenite grain.

The presented above mechanism of the irreversible temper embrittlement effect occurs as long as 'excessive' carbon atoms occurred on grain and subgrain boundaries. These atoms can originate not only from dissolving ϵ carbides but also from a martensitic matrix, which are trying to reach the forming cementite (M_3C) not via a lattice but by grain and subgrain boundaries. This means that the proposed here mechanism of the irreversible temper embrittlement will also function in low-carbon and very low-carbon steels, in which ϵ carbides do not precipitate during tempering. In such case carbon atoms decorating grain and subgrain boundaries will directly originate from martensite.

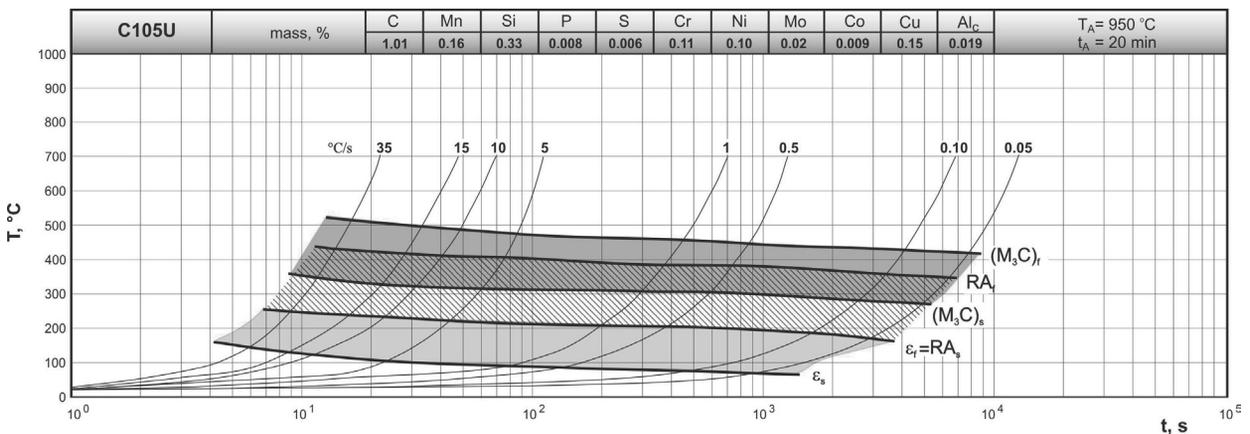


Fig. 1. Continuous Heating Transformations (CHT) diagram of the C105U grade steel (RA - Retained Austenite)

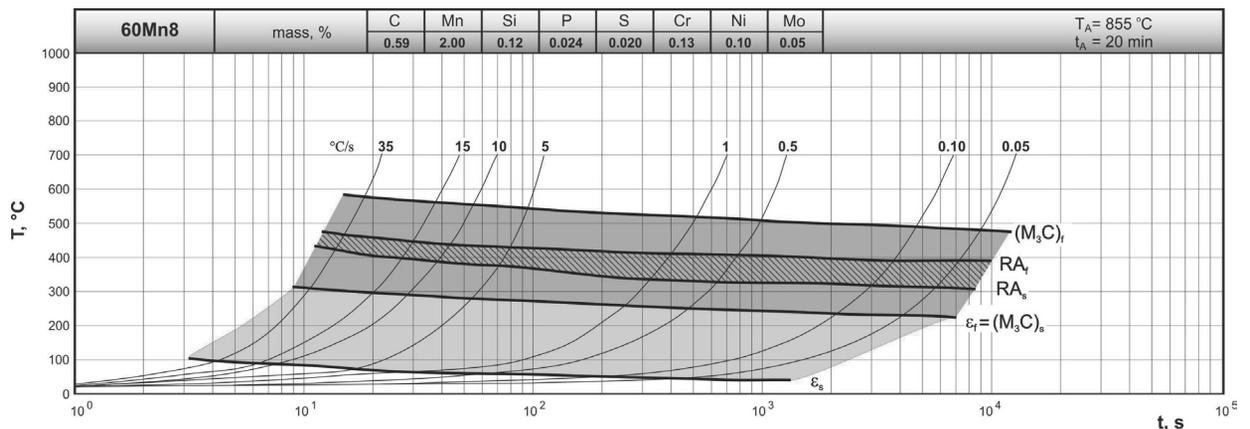


Fig. 2. Continuous Heating Transformations (CHT) diagram of the 60Mn8 grade steel [3]

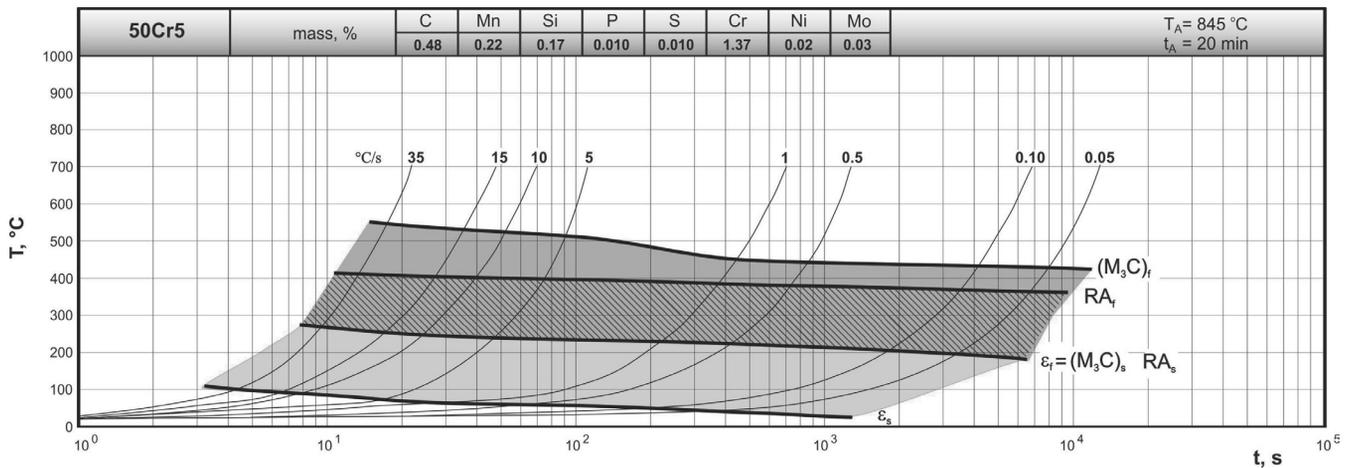


Fig. 3. Continuous Heating Transformations (CHT) diagram of the 50Cr5 grade steel [4]

Decreasing of the fracture toughness due to redistribution of carbon atoms to these boundaries will last as long as the cementite formation (precipitation) process will not be finished. In tempered steels it happens usually at app. 500°C and up to this temperature the ‘lasting’ of the irreversible temper embrittlement is observed, however its intensity above 300°C gradually decreases.

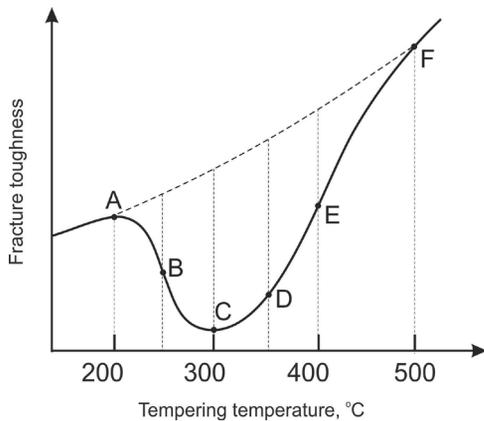


Fig. 4. Scheme of the irreversible temper embrittlement in low-carbon steels

The described above mechanism of formation of the irreversible temper embrittlement works in low-carbon steels, which after quenching do not contain retained austenite, is illustrated in Fig. 4. The characteristic feature is that, then we are dealing only with a harmful influence of the carbon redistribution in the tempered steel structure and that the tempering temperatures range within which the fracture toughness is lowered (range of the irreversible temper embrittlement) is very wide. In unalloyed steels it is between 200 and 500°C (line: ABCDEF) with the highest intensity at app. 300°C. This range is specially interesting for several applications of quenched and tempered steels due to their hardness, however it is not using in practice because of their low fracture toughness.

3. Irreversible temper embrittlement in high-carbon steel

High-carbon steels, after quenching contain supersaturated with carbon brittle martensite and a large volume fraction of the ductile retained austenite. If the martensite fracture toughness corresponds to point G' (Fig. 5), then due to the presence of retained austenite in such steel microstructure its fracture toughness is higher by the segment G'G value. After tempering of such steel at above 200°C, due to solution of large amounts of ε carbides of a formula close to Fe_{2.4}C, in the martensite matrix the local carbon concentration can increase by:

$$12.010 : (55.845 \times 2.4) \times 100 \% = 8.96 \%C \quad (1)$$

where: 12.010 - carbon atomic weight,
55.845 - iron atomic weight,
2.4 - fraction of iron atoms in carbide Fe_{2.4}C.

At such carbon local concentration in a tempered steel the inverse transformation can occur [6] α → γ, which in practice will cause an increase of the retained austenite amount at tempering, with all consequences of this phase increased fraction.

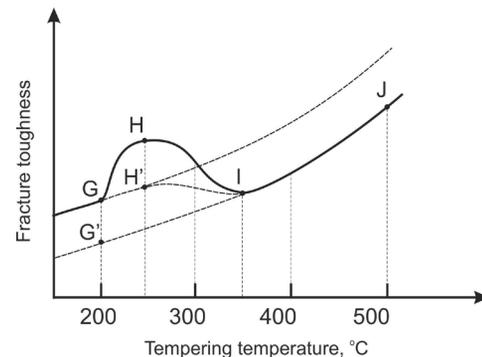


Fig. 5. Scheme of the irreversible temper embrittlement in high-carbon steels

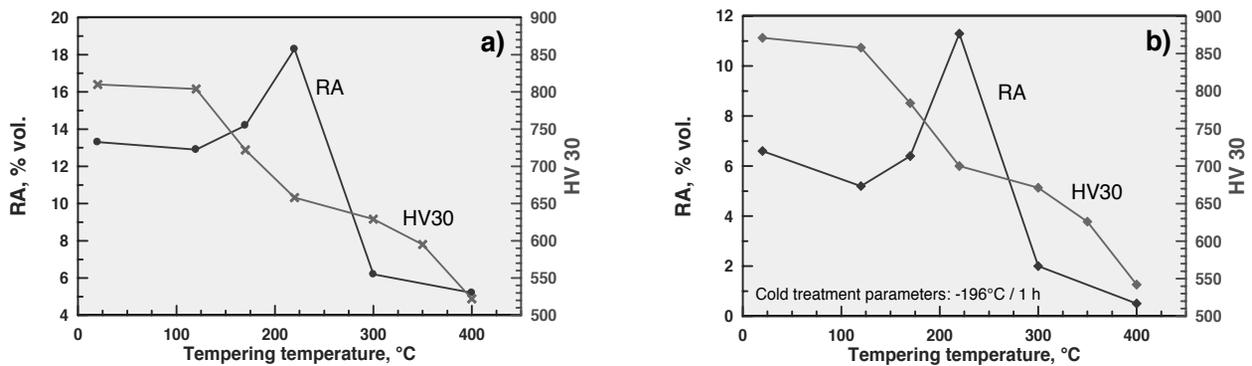


Fig. 6. The influence of tempering temperature on hardness (HV30) and volume fraction of retained austenite (RA) in 70MnCrMoV9-2-4-2 steel after quenching from 820°C: a) without cold treatment, b) after cold treatment (-196°C/1hour), acc. to [7]

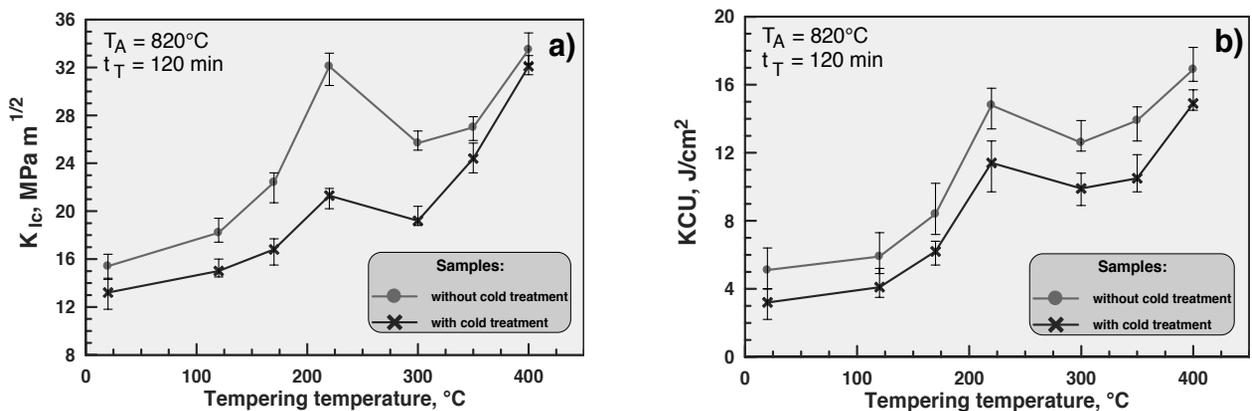


Fig. 7. The influence of tempering temperature of 70MnCrMoV9-2-4-2 steel (by the time 120 min) on the changes of: a) stress intensity factor (K_{Ic}), b) impact strength (KCU2), acc. to [7]

First of all the steel fracture toughness will increase (much more than it would result from an advanced martensite tempering, Fig. 5 - line GH) and its hardness will decrease. Unfortunately these changes occur within rather narrow range of tempering temperatures. Carbides ϵ start their intensive dissolution only above 200°C (and then it is possible to notice a significant increase of the retained austenite fraction) and already above 250°C begins its transformation into lower bainite (it concerns both 'old' and 'new' retained austenite). This transformation finishes at app. 350°C in unalloyed steels (see Fig. 1) and at app. 400°C in alloyed steels (see Figs. 2 and 3). As the result the fracture toughness significantly decreases (Fig. 5 - line HI), which is incorrectly understood as the effect of the irreversible temper embrittlement (on account of the tempered temperatures range: 250-350°C, see Fig. 5). Incorrectness of such interpretation is based on the fact that, in case of an increased austenite fraction, due to dissolving of carbides ϵ at temperatures above 200°C, after tempering in the range 250-350°C, when this austenite is transformed into lower bainite, we are dealing with lowering the fracture toughness - in approximation - to a level which determined the tempered martensite (to G'IJ line in Fig. 5).

We can assume that in such high-carbon steels there is no carbon redistribution to grain boundaries and to cell structure boundaries. Because the characteristic feature of their fractures,

after tempering at 300-350°C, are never intergranular (which is characteristic for irreversible embrittlement) but always transcrystalline.

An example of such steel behaviour during low and middle tempering was found, among others in investigations [7] of 70MnCrMoV9-2-4-2 steel. In Fig. 6 it was shown how during this steel tempering in a temperature range 120-300°C the retained austenite volume fraction increases (RA), both in samples subquenched and not subquenched in liquid nitrogen directly after quenching. Increased of the retained austenite fractions are 'sensible' even by hardness changes. On the other hand it is seen in Fig. 7, that within ranges of the evident increase of the retained austenite fraction the significant fracture toughness increase - measured both by a stress intensity factor K_{Ic} and by impact strength KCU2 - occurs.

4. Irreversible temper embrittlement in medium-carbon steel

Medium-carbon steels containing from 0.25-0.65% C are classic steels for quenching and tempering. After quenching, usually a few percent of the retained austenite are in matrix of

such steels, while the rest constitutes martensite of a middle carbon content. In such case, during tempering in a range 200-500°C there is a simultaneous influence of transformations occurring in both phases existing in these steels. It means, the carbon atoms redistribution in tempered martensite and the increased fraction followed by destabilising and transformation into lower bainite of both 'old' and 'new' retained austenite. Mutual influence of changes occurring in these two phases, leads to such changes in the fracture toughness as shown in the scheme in Fig. 8.

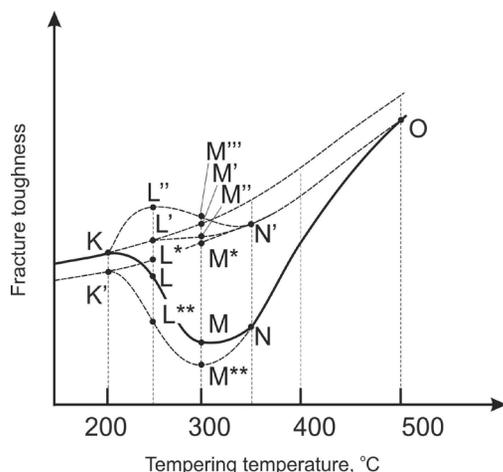


Fig. 8. Scheme of the irreversible temper embrittlement in middle-carbon steels

If the analysed in Fig. 8 steel did not contain the retained austenite but only martensite its fracture toughness after tempering at 200°C would correspond to point K' and changes of its fracture toughness - controlled only by carbon atoms redistribution - would be passing along line: K'L**M**NO, analogous as in Fig. 4. However, due to presence of a few percentages volume of the retained austenite in the quenched matrix, the steel fracture toughness after tempering at 200°C is larger by a value K'K and corresponds to point K. If, in the martensitic part of the steel matrix, due to dissolution of ϵ carbides none carbon redistribution to boundaries of grains and cell structures occurred and if the retained austenite fraction did not increase in relation to dissolving then fracture toughness of the steel at tempering temperature of 250°C would reach point L' value. However, due to increase of the retained austenite fraction, the steel fracture toughness increases by a value (segment) L'L'', while due to carbon redistribution in martensite decreases by a value L*L**. As the result of these two influences, after tempering at 250°C, the fracture toughness will correspond to point L value.

After tempering at 300°C the fracture toughness would match point M'. However due a transformation of the part of 'old' austenite this resistance decreases from point M' to point M'' and due to existing part of 'new' austenite the fracture toughness increases from M' to M'''. In martensitic part of a matrix, as a result of the carbon redistribution the fracture toughness decreases from M* to M**. Finally, after tempering at 300°C, the fracture toughness obtains values corresponding to point M.

After tempering at 350°C when there is no retained austenite in matrix (neither 'old' nor 'new') and there are no benefits from this phase, the fracture toughness of tempered steel is determined by the fracture toughness of tempered martensite (in which carbon atoms, did not yet manage to form cementite and are placing themselves mainly on grain and subgrain boundaries). Thus, it will correspond to point N value.

After tempering at 500°C when the cementite precipitation is ending, the redistribution of the carbon atoms disappears, and only the process of the cementite particles coagulation occurs in the structure of the tempered steel. The matrix recovery process also finishes since it 'is preparing itself' for recrystallisation.

It is important to notice, that in medium-carbon steels (Fig. 8), in which we are dealing with advantageous influencing of certain amounts of the retained austenite (regardless of its transformation), the effect of the fracture toughness decreasing due to carbon redistribution in tempered martensite, is by this retained austenite reduced and narrowed from the side of the higher than 300°C tempering temperatures.

In practice, the schematically presented above changes in the fracture toughness after tempering in a range: 200-500°C can be easily confirmed. However, it should be remembered that the temperature ranges of individual transformations are influenced by alloying elements. Their influence can be determined by means of diagrams of the kinetics phase transformations during tempering, it means CHT diagrams [8-16].

5. Conclusions

The effect of irreversible temper embrittlement is not sufficiently explained. Existing theories of preferential precipitations from martensite along grain boundaries [17], chemical destabilisation [18] and mechanical destabilization [19] of the retained austenite, segregation of admixtures to grain boundaries [20] etc. can be easily invalidated, using modern investigation possibilities of electron, transmission and scanning microscopy.

The proposed in this paper thesis of explanations of this undesirable, known for a long time, effect is based mainly on the research experience of the authors, investigating the fracture toughness as well as phase transformations at tempering. On these grounds as the main reason of the irreversible temper embrittlement the carbon atoms redistribution to grain boundaries and to cell structure boundaries in martensitic part of the matrix, during dissolving of metastable intermediate carbides (mainly carbide ϵ) - was considered.

The retained austenite (if it exists in the quenched steel matrix) increases fracture toughness, but it is only an accompanying effect, without any influence on intergranular (and rather intercellular) character of fractures characteristic for this type of brittleness.

In view of a domination of influences of significant amounts of carbon atoms placed in a privileged way along grain and cell structures boundaries (redistributed), eventual influences of admixture atoms (being in thousandth parts of percentage) on the fracture toughness decreasing after tempering at 200-500°C, seems to be overestimated.

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