Available online at www.sciencedirect.com

SciVerse ScienceDirect

Scripta Materialia 68 (2013) 945–948

Scripta MATERIALIA

www.elsevier.com/locate/scriptamat

Interrupted ageing in steels: Hardness improvement and microstructural stabilization

B. Kim,[a] C. Celada,[b] D. San Martín,[b] J. Chao,[b] J. Vara[b] and P.E.J. Rivera-Díaz-del-Castillo[a,*]

[a] *Department of Materials Science and Metallurgy, University of Cambridge, Pembroke Street, Cambridge CB2 3QZ, UK*
[b] *MATERALIA Group, Department of Physical Metallurgy, Centro Nacional de Investigaciones Metalúrgicas (CENIM-CSIC), Av. Gregorio del Amo 8, 28040 Madrid, Spain*

Received 6 February 2013; revised 12 February 2013; accepted 16 February 2013
Available online 27 February 2013

Similarly to aluminium alloys, interrupted ageing in steels may increase hardness by 10%. By adding an intermediate stage between quenching and tempering, where quenched martensite is left to age at room temperature, carbon forms finer precipitate microstructures, which become more stable at room temperature. Using thermoelectric power to model carbon segregation to dislocations, it appears that room temperature ageing increases the number of effective nucleation sites for the subsequent tempering stage, as reflected in the microstructure and hardness.

Keywords: Ageing; Martensitic steels; Interstitial diffusion; Hardness; Carbides

In freshly quenched martensite, where the diffusion of solutes is restricted because of slow kinetics at room temperature, only interstitials such as carbon and nitrogen diffuse significantly. The distribution of carbon atoms immediately after quenching has a marked effect on the subsequent heat treatment [1]. It is understood that in freshly quenched martensite, carbon becomes trapped by defects, such as dislocations, as these display a strain field to which solutes such as carbon become attracted. Carbon atoms gather in the vicinity of the dislocation forming the so-called Cottrell atmospheres, cancelling the dislocation strain, resulting in a pinning effect [2]. The present work introduces an intermediate stage between quenching and tempering, called interrupted ageing (IA). During this stage, the freshly quenched martensite is left to age at room temperature, allowing for controlled carbon segregation into dislocations, resulting in increased hardness and more stable precipitate structures.

A technique that has been employed in order to study carbon-controlled reactions, such as precipitation, is thermoelectric power (TEP) [3–8]. The main benefit of TEP is attributed to its sensitivity in detecting atoms in solid solution, which can be exploited for tracking the kinetics of carbon diffusion during IA. TEP measurements, combined with the model originally devised by Kalish and Cohen [1], provide further understanding of the interrelationship between processing, microstructure and the mechanical properties of mid-carbon steels undergoing IA.

An automotive industrial grade of composition Fe–0.55C–1.6Si–0.7Mn–0.5Cr–0.13V (wt.%), where Cu, Ni and Mo were present as tramp elements, was used in this study. The as-received material was in the form of rods, with an initial hardness of 317 HV1. The specimens were heat treated in an Adamel Lhomargy dilatometer (model DT1000) in order to study interruption, tempering time and temperature. The specimens were cylindrical rods 3 mm in diameter and 12 mm in length. The heat treatment was carried out as shown in Table 1.

T_1 and t_1 are the austenitization temperature and time, respectively; T_2 and t_2 are the tempering temperature and time, respectively; and t_{IA} is the duration of the room temperature interruption. For all conditions, the samples were heated at a rate of 10 °C s^{-1}, austenitized for 180 s, quenched to 55 °C using helium flux at 300–500 °C s^{-1}, held for 60 s and then allowed to cool down to room temperature. The samples undergoing IA were removed from the dilatometer and left to age at room temperature before the subsequent tempering stage.

* Corresponding author. Tel.: +44 (0) 1223334300; e-mail: pejr2@cam.ac.uk

1359-6462/$ - see front matter © 2013 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.scriptamat.2013.02.036

Table 1. Heat treatment summary for the nine conditions investigated.

	T_1 (°C)	t_1 (s)	t_{IA}	T_2 (°C)	t_2 (s)
L1	880	180	7.2 h	250	1800
L2	880	180	3 days	250	1800
L3	880	180	30 days	250	1800
L4	880	180	30 days	250	300
L5	880	180	–	–	–
L6	880	180	–	250	1800
L7	880	180	–	250	5400
L8	880	180	–	300	1800
L9	880	180	30 days	300	1800

The critical transformation temperatures were determined from dilatometry as $Ac_1 = 798 \pm 3$ °C and $Ac_3 = 832 \pm 3$ °C, $M_s = 238 \pm 9$ °C, where Ac_1 and Ac_3 are the austenitization start and finish temperature, and M_s is the start temperature. These are the average values of 10 different experiments. The prior austenite grain boundaries were revealed by the thermal etching method [9], and an average grain size of 5 ± 1 μm was estimated from light optical micrographs, using the mean linear intercept method [10].

After heat treatment, the samples were characterized using transmission electron microscopy (Philips CM30 model). Over 500 intralath precipitate particles were analysed per condition, taken from three to four different TEM frames, all under the same magnification, ×52k. The length, width and centre-to-centre particle spacing were measured. Having applied stereological corrections [11], the shape of the carbide was approximated to a cylinder, from which the equivalent radius of a sphere was extracted. This was carried out for comparison purposes only, as the aspect ratio varied slightly throughout the different conditions. Vickers hardness tests were carried out using a Mitutoyo MVK-H2 microhardness indenter with a 1 kg load.

Representative microstructures are shown in Figure 1a for conditions L3, L6, L8 and L9. Following detailed microstructural analysis, the particle size and spacing relationship are shown in Figure 1b. The general trend observed is that particle size decreases with increasing temperature, whereas particle spacing decreases with the interruption time.

As a way of ensuring that the microstructures of the two conditions were statistically distinct, Kolmogorov–Smirnov (K–S) statistical tests [12] were carried out (not presented in here). Given two precipitate size distributions, x_1 and x_2, the K–S test states the null hypothesis that x_1 and x_2 are from the same continuous distribution. The output of the test is either a 1 or a 0, where 1 rejects the null hypothesis, i.e., x_1 and x_2 are not from the same continuous distribution, and 0 infers a valid hypothesis. Based on Figure 1b and confirmed by the outcome from the K–S test, the observed trend was that IA results in a finer microstructure in terms of smaller particle size and spacing (L3 vs. L6 and L9 vs. L8), and that the duration of tempering (t_2) after 30 days of IA did not influence the microstructure (L3 vs. L4). Tempering at a higher temperature after IA led to smaller carbides, without altering their spacing (L3 vs. L9).

The IA stage leads to finer microstructures; it can be postulated that IA provides a more efficient take-up of

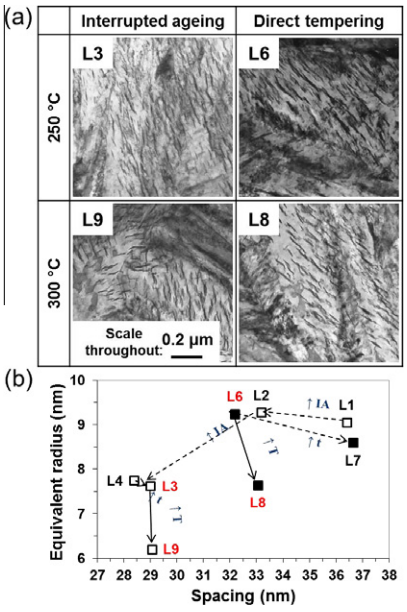

Figure 1. (a) Representative bright-field images shown for conditions L3, L6, L8 and L9, and (b) particle size and spacing represented on a grid, where the arrows labelled "t", "IA" and "T" indicate an increase in tempering time, interruption time and tempering temperature, respectively.

carbon atoms from the solid solution. During the time at room temperature, the carbon atoms are likely to diffuse into defect traps, such as dislocations. Allowing segregation into dislocations increases the number of effective nucleation sites for the tempering stage, evidenced in the finer microstructure obtained (L3 vs. L6 and L9 vs. L8).

Differences in hardness were observed for the same conditions over a period of 6 months (Figure 2). The percentage hardness variation for each condition is shown on top of the bars. The error bars represent one standard deviation. The biggest change during the 6 months is observed in L6, followed by L7. Since both were tempered at 250 °C, it follows that the tempering reaction does not come to completion at 250 °C, and so continues at room temperature at a slower pace, a phenomenon that has been reported in the literature [13]. This is further consistent with the fact that the change observed in L8 is less than that in L6, where L8 having been tempered at 300 °C would have reached a higher degree of reaction completion than L6, which was tempered at 250 °C.

Condition L9 shows distinctive behaviour: the introduction of IA increases hardness with respect to L8, but

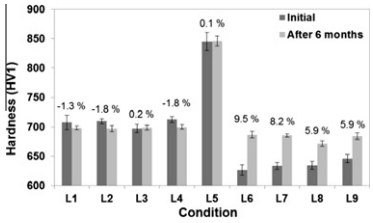

Figure 2. Hardness changes over 6 months.