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CARBON ENRICHMENT IN RESIDUAL AUSTENITE DURING MARTENSITIC TRANSFORMATION

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Abstract

Carbon enrichment of austenite and carbide precipitation during martensitic transformation have been investigated in three novel low-carbon steels. Significant partitioning of carbon into retained austenite was observed in the final microstructure, because of the relatively high martensite-start temperatures. The fact that the autotempering is associated with very fine cementite precipitates within the martensite probably helps in achieving the observed ductility in spite of the high-strength when compared with reported data on the tensile properties of quenched martensitic steels.

1 Introduction

The stabilisation of austenite due to carbon partitioned during martensite formation has been successfully exploited in the design of transformation-toughened steels [1-8]. Much of this research has been associated with carbon partitioning from bainite into austenite. There is a limited amount of work to indicate that the thin films of austenite associated between plates of martensite also enrich with carbon [9-11] and there has been recent work to exploit this process in the design of 'quench and partitioning' steels [12, 13]. In the latter case samples containing both untempered martensite and retained austenite are warmed in order to permit the carbon to partition into the austenite.

We report here on some experiments conducted to develop silicon and aluminium containing steels in which the austenite is enriched with carbon during the quench itself. This is in competition with processes that lead to autotempering and the precipitation of carbon as carbides.

2 Experimental Procedure

The chemical composition of the three experimental steels are listed in Table 1. They were all made as 50 kg vacuum melts and hot-rolled. Subsequent heat-treatment was applied to the steels as illustrated in Fig. 1. The hot-rolled sheets were cut into 180×40×3 mm plates, treated in a box-furnace and quenched into a mixture of water and 20% polymer (Dyna GCOL-E) mixture for mechanical testing. The temperature was in all cases monitored using a thermocouple welded to the samples. A precision dilatometer was used, together with the offset method for interpreting the transformation temperatures, as described elsewhere [14]; the dilatometer sample dimensions were 3×3×10 mm.

Tensile tests were conducted on samples with a gauge length of 50 mm, width 25 mm and thickness 3 mm at a strain rate of 0.2 min^{-1}. Field emission gun scanning electron microscopy was conducted using a *Zeiss Ultra 55* microscope operating at 1-5 kV with a working distance of 2-4 mm to take advantage of the in-lens detector. For this, the samples were etched lightly with 2% nital. Focused ion beam (FIB) has been used to prepare the transmission electron microscopy (TEM) samples in the selected area. The cut sample size is about 0.05×4×5 μm. The analysis was performed in a Philips CM200 transmission electron microscope operated at 200 kV.

X–ray diffraction was performed on 1.5 mm thick specimens polished using 6 μm diamond paste and chemically polished using 5% HF+ 50% H_2O_2 + 45% H_2O mixture. The diffraction covered 2θ from 35-110° with a 10s step of 0.02°, using CuK_α radiation. Reitveld analysis [15] and Reitveld cell refinement [16, 17] were used to calculate the retained austenite content and lattice parameters; these procedures were implemented using the *TOPAS 2.1* software. The carbon concentration x_γ of the austenite was estimated from the lattice parameter a_γ using the equation [18]:

$$x_\gamma = \left(a_\gamma - 0.3570\ \text{nm}\right) 3.8 \times 10^{-3}\ \text{wt\%} \tag{1}$$

Table 1. Compositions of the steels studied, wt%. The Ac_1 and Ac_3 temperatures were measured for a heating rate of 2 °C s^{-1}.

Steel	C	Si	Mn	P	S	N	Al	B	Mo	Nb	Ti	Ni
A	0.153	0.78	1.54	0.012	0.0029	0.0045	0.43	0.0014	0.21	0.016	-	-
B	0.242	0.29	1.47	0.011	0.0011	0.0025	0.51	0.0026	-	-	0.02	-
C	0.252	0.78	1.29	0.011	0.0012	0.0030	0.30	0.0025	-	-	0.02	0.3

Steel	Ac_1/ °C	Ac_3/ °C
A	759±3	928±1
B	737±1	854±1
C	746±3	855±2

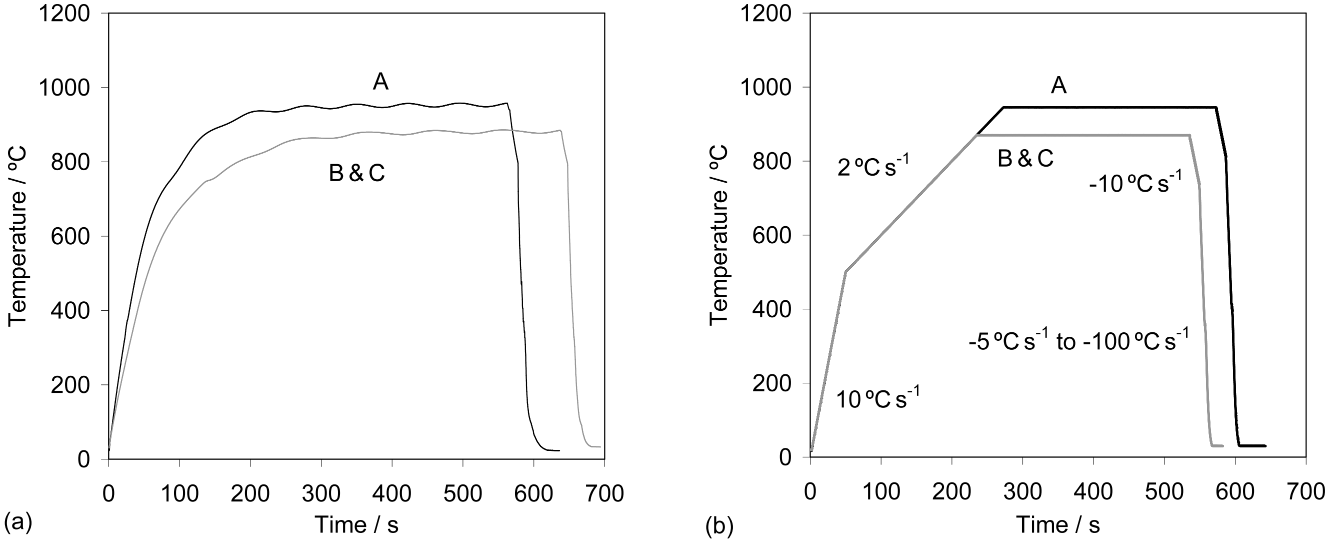

Figure 1. Heat treatments: (a) in a box furnace for mechanical test samples, (b) in a dilatometer.

3 Results and Discussion

Cooling rates in excess of about 30 ºC s^{-1} were found to be sufficient to avoid transformation prior to the formation of martensite, as illustrated in Fig. 2 which shows plots of the dilatometrically measured transformation temperature and the sample hardness as a function of the cooling rate. The critical cooling rate corresponding to the first transformation being martensite is given by the rate beyond which both of these parameters reach a stable value. Also illustrated are the calculated martensite-start temperatures [19, 20] and calculated martensite hardness [21] which seem to agree reasonably well with those measured.

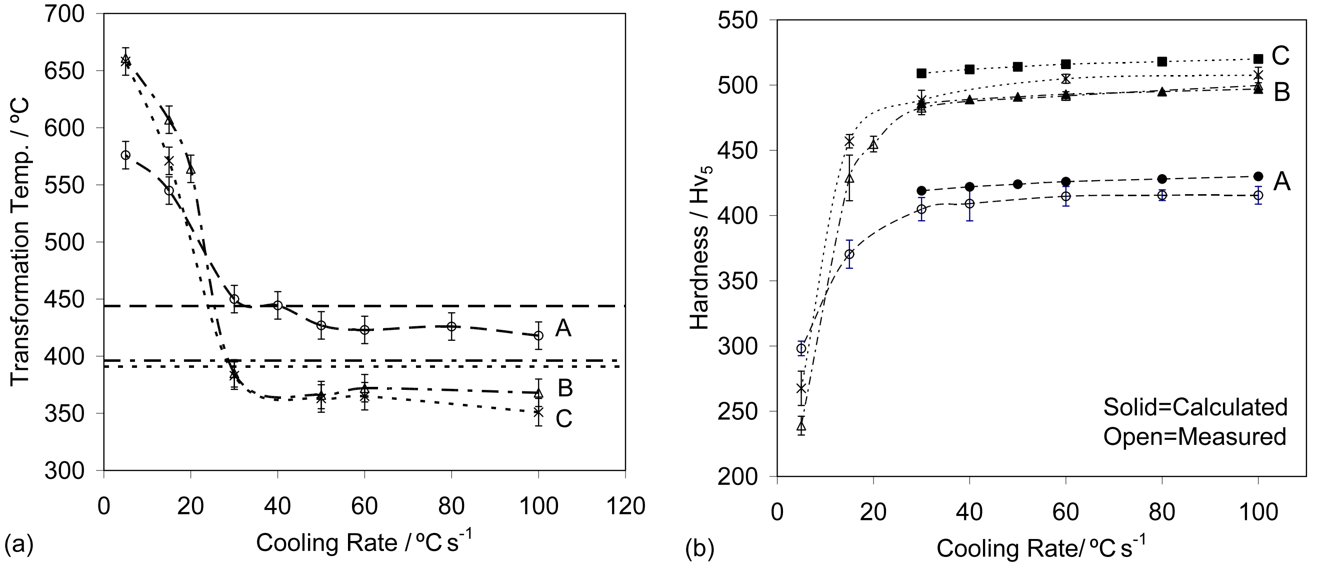

Figure 2. Measured transformation temperature and hardness as a function of the cooling rate. The horizontal lines in (a) show the calculated martensite-start temperatures [19, 20], at 444, 394 and 391ºC for steels A, B and C respectively. The calculated martensite hardness values [21] are also presented in (b).

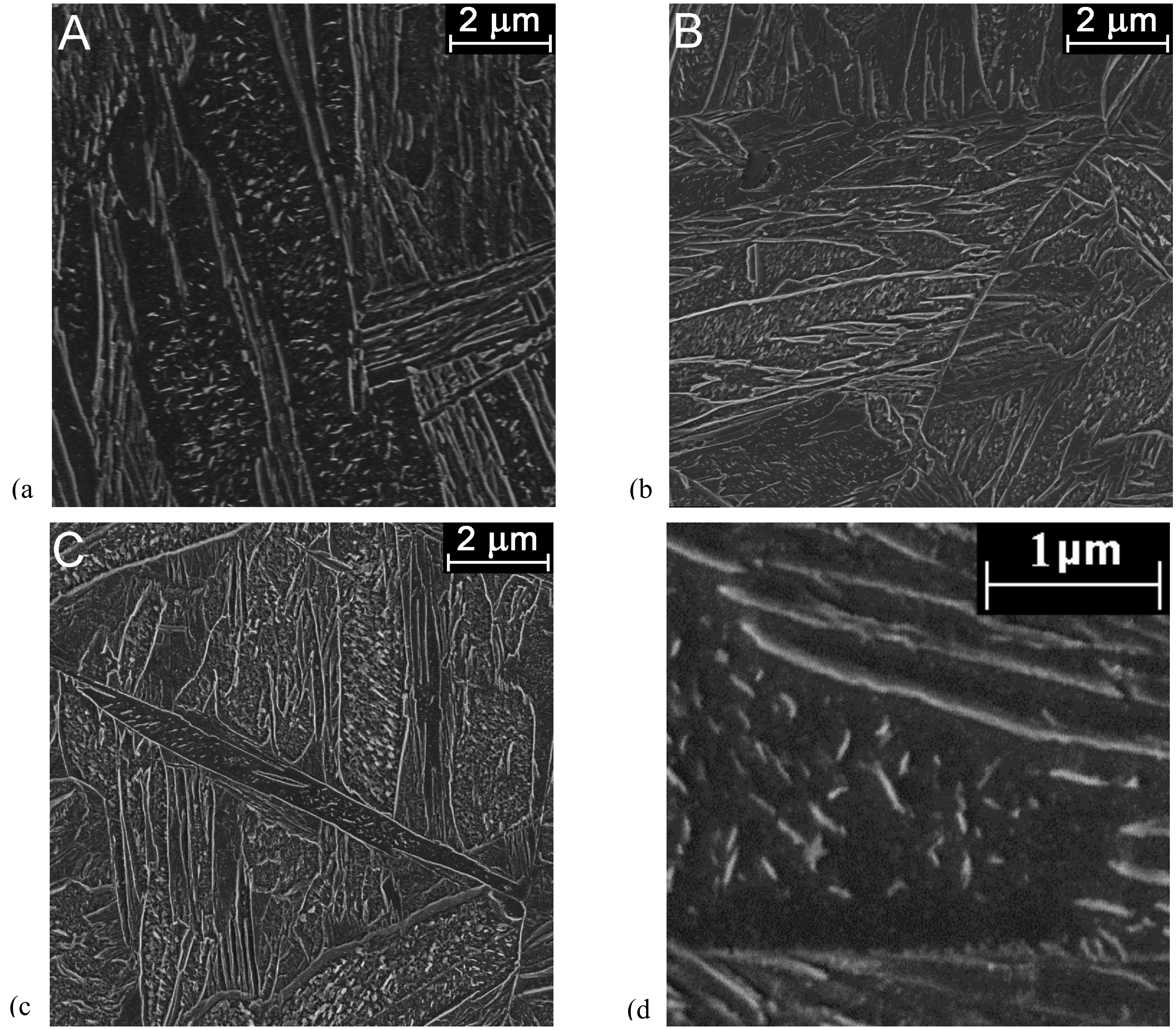

Figure 3. (a) Steel A, 945ºC for 5 min followed by quenching into a water/polymer solution. (b)Steel B, 870ºC for 5 min followed by quenching. (c) Steel C, 870ºC for 5 min followed by quenching. (d) Steel A, showing the precipitate–free zone at the edges of the plate of martensite, with coarser carbides towards the centre.

Fig. 3 shows the microstructures of the three steels after quenching from their respective austenitisation temperatures; they illustrate the typical features of autotempered martensite [22], but the following points are noteworthy. Carbide precipitates are coarsest towards the centres of the martensite plates, and there appears to be a precipitate–free zone towards the edges of the plates (Fig. 3d). This indicates a competition between carbide precipitation and the partitioning of carbon as the martensite cools below its martensite-start temperature M_s [23].

It was confirmed that the carbide formed during autotempering is cementite. Fig. 4 shows a dark field image and the indexed diffraction pattern of the cementite obtained in as-quenched steel A. Two kinds of cementite morphologies were observed. The coarser cementite (fig. 4a) has an elongated shape while the finer particles (fig. 4c) are globular in shape. Both selected diffraction patterns show that the cementite obeys the Bagaryatski orientation relationship with martensite. Difference in cementite morphologies observed is due to the different in transformation temperature. With volume fraction of martensite depending on decreasing temperature, it is expected that cementite form in the martensite lath that form first (at high temperature) is coarser compare to the one that form at the end of martensite transformation (at low temperature).

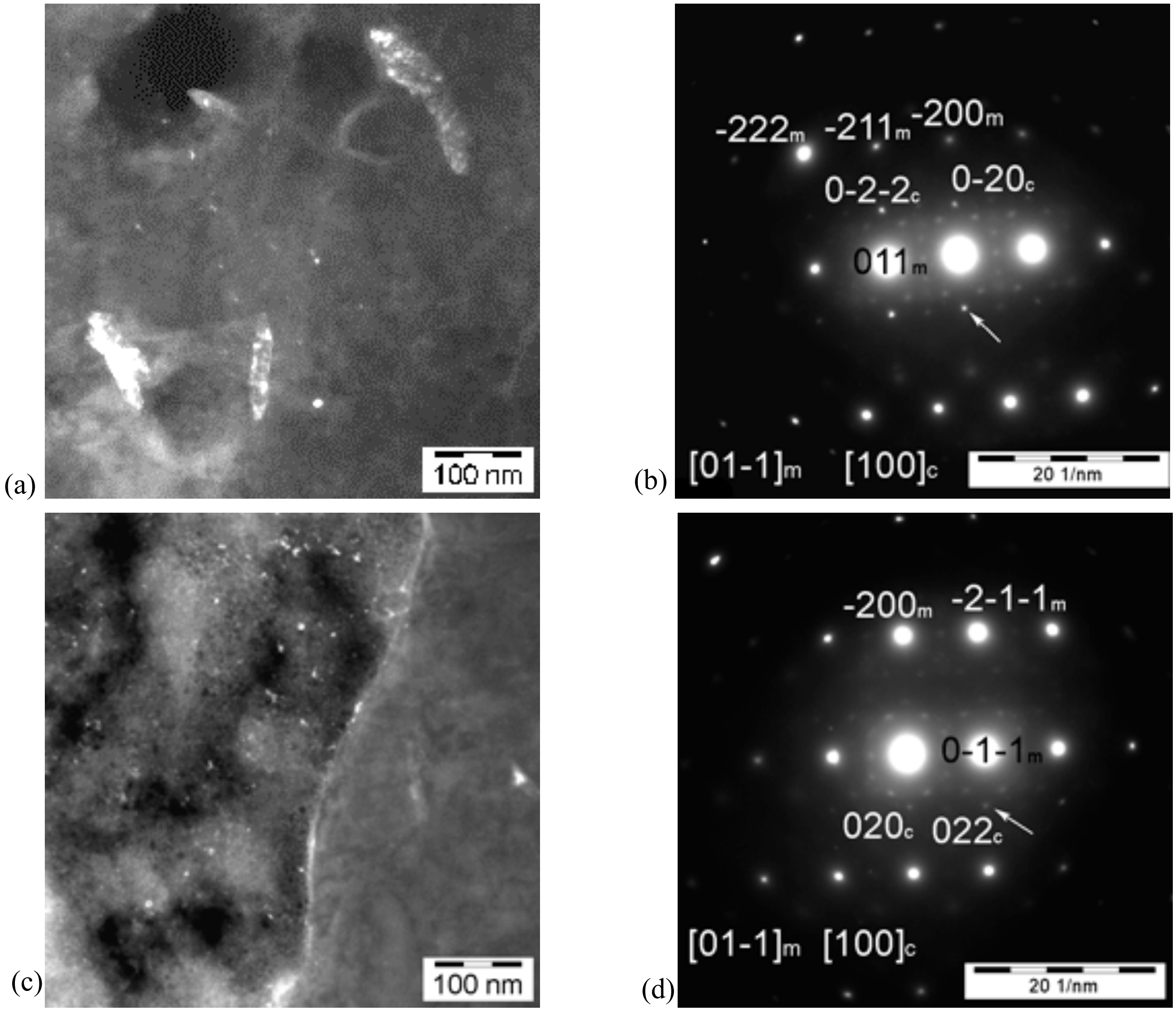

Figure 4. (a) Dark field image of cementite precipitation obtained in as quenched steel A, using the spot indicated in (b). (c) Dark field image of a fine cementite precipitation obtained from the same sample, using the spot indicated in (d).

3.1 Retained Austenite

The characteristics of retained austenite are illustrated in Fig. 5a. All of the steels contain approximately 4-5 vol.% of retained austenite, independent of the cooling rate. The measured carbon concentration x_γ of the austenite is much higher in each case than that of the steel as a whole. This carbon concentration is mostly insensitive to the cooling rate and it is interesting that Steel A has the largest concentration. As mentioned previously, there is a competition between the processes of carbon partitioning from the martensite into the residual austenite, and the precipitation of excess carbon in the martensite. Steel A not only has the highest martensite-start temperature (which facilitates partitioning) but also the lowest carbon concentration (which reduces the driving force for precipitation); the greater x_γ in steel A is therefore attributed to these two factors. All of these factors can be taken into account as described elsewhere [24]; the results for the time taken to decarburise a plate of thickness 0.25 μm is illustrated in Fig. 5b. It is evident that the process will be faster for steel A, consistent with its greater value of x_γ.

Having described the retained austenite, it is unlikely that this small fraction contributes perceptibly to the mechanical properties [25, 26]. The main outcome is that the composition of the austenite is consistent with autotempering and indeed with the observation of the precipitate free zones at the peripheries of autotempered plates of martensite. However, it is clear that the autotempering has resulted in a considerable amount of ductility prior to failure, in spite of the high strength, as illustrated in Fig. 6a. Figure 6b compares the mechanical properties obtained in this study to published data of quenched martensite [27-49]. Note that the mechanical properties of the investigated steels have better elongation compared to all data based on flat tensile-test specimens. Table 2 shows the chemical composition range and the test specimen dimensions obtained from [27-49].

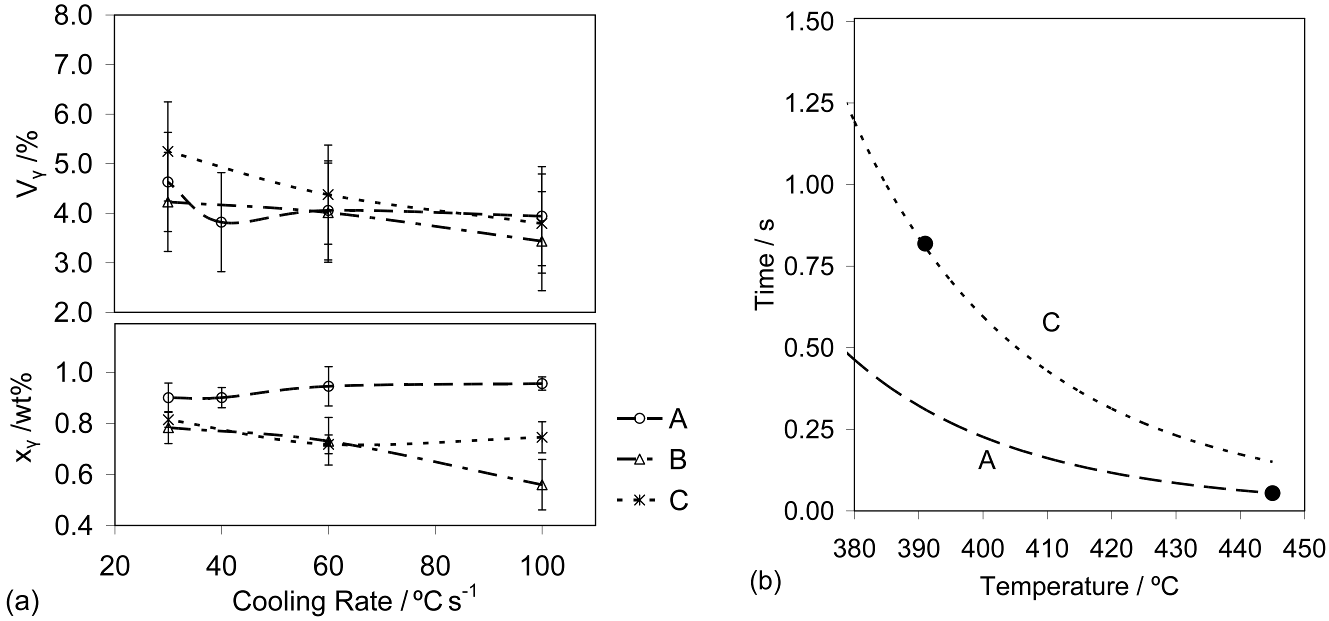

Figure 5. (a) Volume percent V_γ (%) of retained austenite and its carbon concentration x_γ (wt%) as a function of the cooling rate for steels A, B. and C. (b) Time to decarburise a plate of thickness 0.25 μm. The M_S temperature is indicated by the point on each curve. The results for steel B were almost identical to those of C and hence are not plotted.

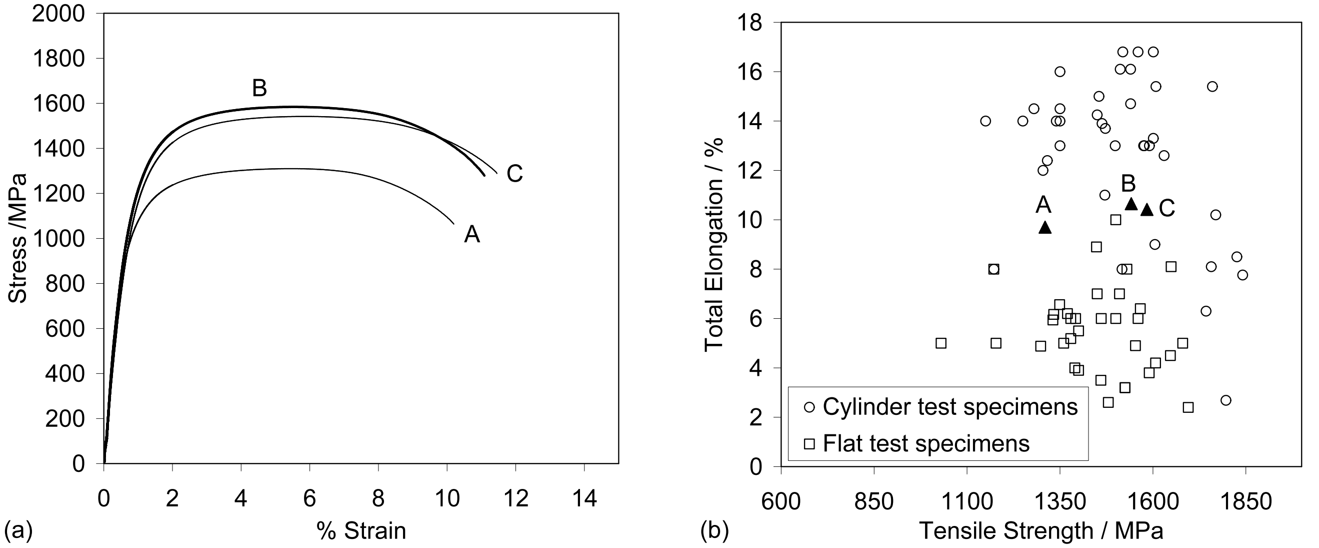

Figure 6. (a)Engineering tensile-stress versus engineering strain curves for the three steels. (b) Mechanical properties of the novel steels compare to the mechanical properties of the as-quenched martensite in the literature [27-49].

4 Conclusions

In a series of steels designed to be used in the as-quenched state, autotempering led to good mechanical properties without the application of subsequent heat treatment. It has been shown that the autotempering manifested both in terms of carbide precipitation and the carbon enrichment of small quantities of retained austenite in the microstructure which may be responsible for the observed increase ductility.

Table 2. The chemical composition range and the test specimen dimension of the as quenched martensitic used in figure 6b.

Composition/ wt%	Range
C	0.09-0.26
Mn	0.08-2.5
Cr	0-4.1
Mo	0-0.79
Si	0.03-1.81
Ni	0-4.09
Al	0.014-0.07
Ti	0-0.155
Nb	0-0.12
V	0-0.044
Cu	0-0.13
W	0-9
B	0-0.003
P	0.004-0.14
S	0.0036-0.08
N	0.0008-0.0087
Specimens dimension	
Thickness (flat specimen)	1-3.5mm
Diameter (cylinder specimen)	5-10mm

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