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Physical metallurgy and mechanical behaviour of FeCrWTaV low activation martensitic steels: Effects of chemical composition

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Abstract

This paper essentially deals with chemical composition effects on metallurgical and mechanical behaviour of Fe–7.5/11CrWVTa low activation martensitic steels. Materials investigated are experimental alloys as well as large-scale heats having different contents of Cr (7.5–11%), Ta (0–0.1%), W (0.8–3%) and interstitial elements, like carbon (0.09–0.17%) and nitrogen (0.004–0.045%). For this purpose, phase transformation during heating and cooling have been investigated in anisothermal and isothermal conditions to establish the corresponding Continuous Cooling Transformation (CCT) and Time–Temperature-Transformation (TTT) diagrams. Austenitisation (normalisation) and tempering treatments were performed in a wide range of temperatures. Tensile and impact properties as a function of composition and metallurgical conditions have been determined and compared to 9Cr–1Mo conventional martensitic steels.

1. Introduction

The approach adopted in the development of low activation martensitic materials has involved the substitution of the principal alloying elements such as molybdenum, niobium and nickel in existing commercial steels, by elements which exhibit a lower radiological impact such as tungsten, vanadium, manganese and tantalum [1–3].

The physical metallurgy of commercial high chromium martensitic steels, including the effects of chemical composition, heat treatments and cold-working on transformation characteristics, precipitation and mechanical properties, has been extensively studied [4,5].

The objective of the present work was to implement similar studies on reduced activation martensitic steels to get a better understanding of the composition–microstructure-properties relationship in order to optimise their performances.

This paper is specially focused on the effects of the chemical composition in relation to the phase transformation behaviour, austenitisation and tempering treatments and mechanical properties. For this purpose, a series of FeCrWTaV experimental heats have been investigated and compared to 9Cr conventional martensitic steels.

2. Materials

Low activation (LA...) experimental steels have been supplied by AEA-Culham as cast ingots (50 kg each) [6], which were subsequently hot and cold-rolled into 3.5 mm thick plates.

F82H and JLF-1 steels are studied in the frame of the IEA international collaborative program. They were produced as large-scale heats of 5 and 1 tons respectively and were supplied as plates (7.5 and 15 mm thick) in the N&T condition, that is normalisation at 1050°C and tempering at 750/780°C for 1 h [7]. Their chemical composition is given on Table 1.

LA steels based on a 9Cr–0.8W–0.1Ta matrix, LA12Ta, higher C and N, allow us to study the effect of

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Table 1
Chemical composition of LA martensitic steels (wt%)

Steel	C	Si	Mn	Cr	V	W	N	Ta
LA12Ta	0.155	0.03	0.88	9.86	0.28	0.84	0.0430	0.10
LA12TaLN	0.165	0.02	0.84	9.04	0.24	0.75	0.0048	0.10
LA12TaLC	0.090	0.03	1.13	8.80	0.30	0.73	0.0190	0.10
LA12LC	0.089	0.03	1.13	8.92	0.30	0.73	0.0350	0.01
LA4Ta	0.142	0.03	0.78	11.08	0.23	0.72	0.0410	0.07
LA13Ta	0.179	0.04	0.79	8.39	0.24	2.79	0.0480	0.09
F82H	0.087	0.10	0.21	7.46	0.15	1.96	0.0059	0.023
JLF-1	0.106	0.05	0.52	8.70	0.18	1.91	0.0280	0.08

low carbon (LA12TaLC) and low nitrogen (LA12TaLN) contents as well as the increasing concentration of Cr (LA4Ta, 11Cr–0.8W–0.1Ta) and W (LA13Ta, 9Cr–3W–0.1Ta). Effects of tantalum addition could be analysed by comparison of LA12TaLC and LA12LC behaviour.

F82H and JLF-1 heats are essentially low carbon steels with intermediate W content (about 2%) and lower Cr level in the case of F82H.

3. Experimental procedure

Phase transformations occurring during heating and cooling were investigated by dilatometric techniques. Heat treatments have been conducted under inert gas atmosphere to avoid decarburisation. Austenitisation and tempering anneals were performed respectively in the range 900–1150°C for 30 min and 20–800°C for 1 h.

Microstructure has been characterised by optical microscopy, SEM and Vickers hardness. Prior austenitic grain sizes have been measured by image analysis according to the procedure described in [8].

Specimens for mechanical tests were obtained parallel to the rolling direction of plates. Tensile tests were carried out with cylindrical specimens of 3 mm in diameter and 18 mm of gauge length. The strain rate used was 5×10^{-4}/s.

Impact tests have been conducted on Charpy V-notch specimens of 55 mm long, 10 mm wide and 3.5 mm thick. To obtain full transition curves, tests were performed over the temperature range −200–+400°C. The Ductile–Brittle Transition Temperature (DBTT) corresponds to 50% ductile-50% cleavage fracture mode estimated from force-time curves. DBTT accuracy is about ± 10°C. Energy values were normalised to the initial cross-section area (8×3.5 mm^2) of Charpy specimens.

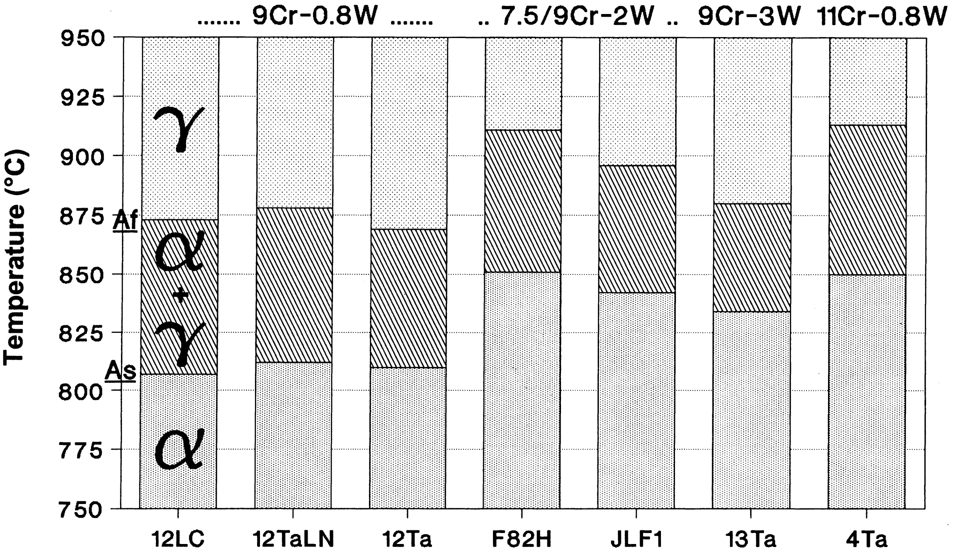

Fig. 1. Temperatures to start (As) and to finish (Af) the transformation of ferrite/martensite (α) into austenite (γ) measured on-heating at 0.008–0.01°C/s.

4. Results

4.1. Phase transformations

The temperatures of phase transformation under heating and cooling have been measured for heating/cooling rates ranging from 0.001°C/s (5°C/h) to 100°C/s, to establish the corresponding phase transformation diagrams. Kinetic features were investigated from isothermal phase transformation conditions. Transformation behaviour has been extensively discussed in Ref. [9] and the main results are reported here.

Fig. 1 shows As/Af temperatures, the boundaries of ferrite/martensite-field (α) and austenite-field (γ), which were determined during heating at the lowest rates used, i.e. 0.008–0.01°C/s. Alloys 9Cr–0.8W (high/low C, no/with Ta) exhibit nearly the same transformation temperatures, which means that interstitial and Ta contents have no significant effects on transformation behaviour during heating. In contrast, higher transformation temperatures are obtained for materials with higher concentrations of W (2–3%) and Cr (11%).

For all materials, Continuous Cooling Temperature (CCT) diagrams exhibit two main phase-fields: an extended martensitic field and a ferritic one. No bainitic reaction was detected. Fig. 2 shows the CCT diagrams determined for F82H steel austenitised for 30 min at 1050°C. The martensitic and the ferritic fields are separated by two critical cooling rates, i.e., R_m the minimal rate to obtain a total transformation of austenite into martensite and R_f the maximal rate to produce a complete transformation of austenite to ferrite. Table 2 summarises R_m and R_f values corresponding to different steels. The differences of R_m values is mainly related to the differences in the prior austenite grain size. Fine grain structures display higher critical cooling rates.

Table 2
Critical rate values for the austenite transformation under continuous cooling

Steel	R_m(°C/h)	R_f(°C/h)
LA12Ta	140	20
LA12TaLN	200	80
LA12TaLC	90	25
LA12LC	45	10
LA4Ta	150	45
LA13Ta	85	22
F82H	60	15
JLF-1	150	50

R_m: minimal cooling rate to obtain a fully martensitic material.
R_f: maximal cooling rate to obtain a fully ferritic material.
Values obtained after austenitisation for 30 min at 1050°C.

The martensite start temperature Ms ranges from 320°C to 430°C and is mainly correlated to the

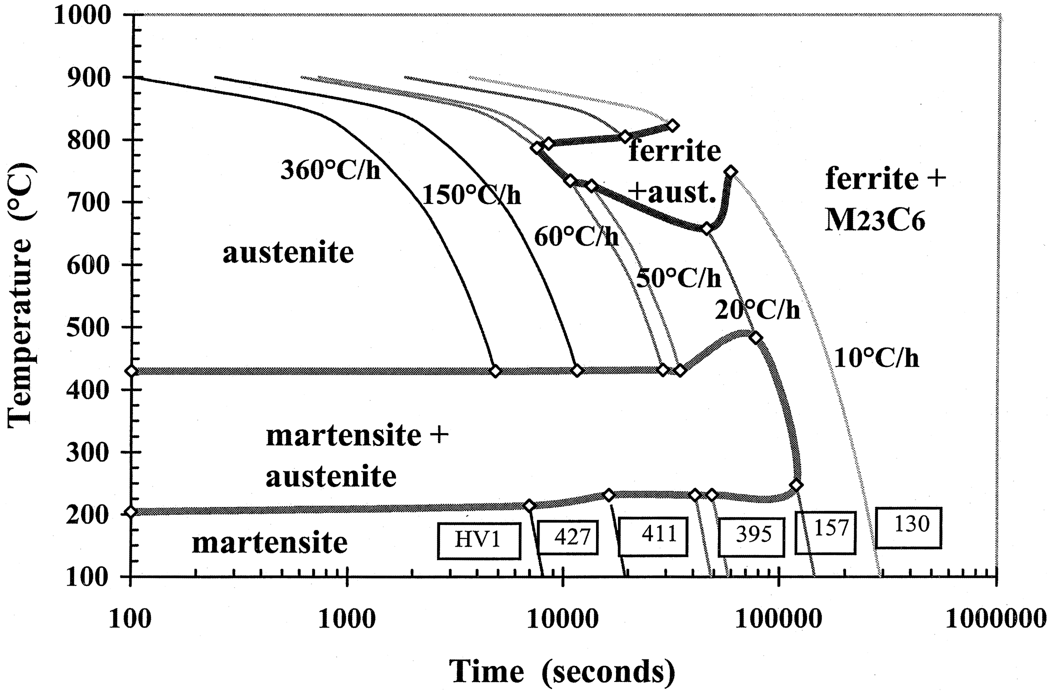

Fig. 2. CCT diagram of F82H steel (7.5Cr–2WTaV, low C) determined after austenitisation for 30 min at 1050°C.

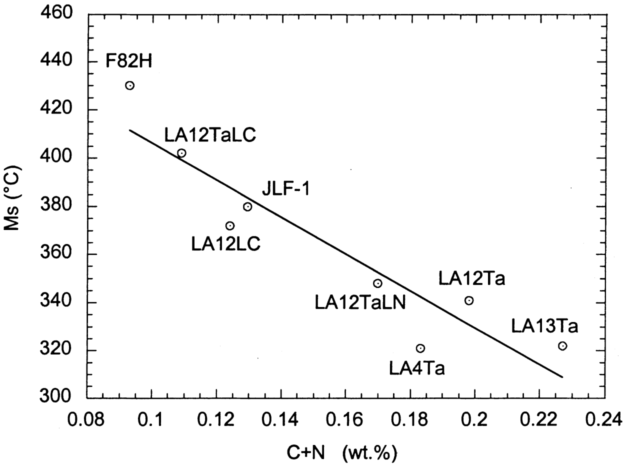

Fig. 3. Martensite start temperature Ms measured during quenching as a function of (C + N) interstitial content.

interstitial content of steels as shown in Fig. 3. The higher Ms values are obtained for the lower C containing steels (370–430°C) and the lower Ms (320°C) corresponds to LA4Ta (11%Cr, high C/N) and LA13Ta (3%W, high C/N) materials.

Time–Temperature–Tranformation (TTT) diagrams have been established after austenitisation for 30 min at 1050°C and cooling down at 150°C/s to the temperature where the isothermal transformation of austenite to ferrite was studied, that is in the range 625–800°C.

The sigmoidal curves describing the transformed austenite fraction Y as a function of the time t at a given temperature, have been fitted using the relation of Johnson–Mehl–Avrami [10].

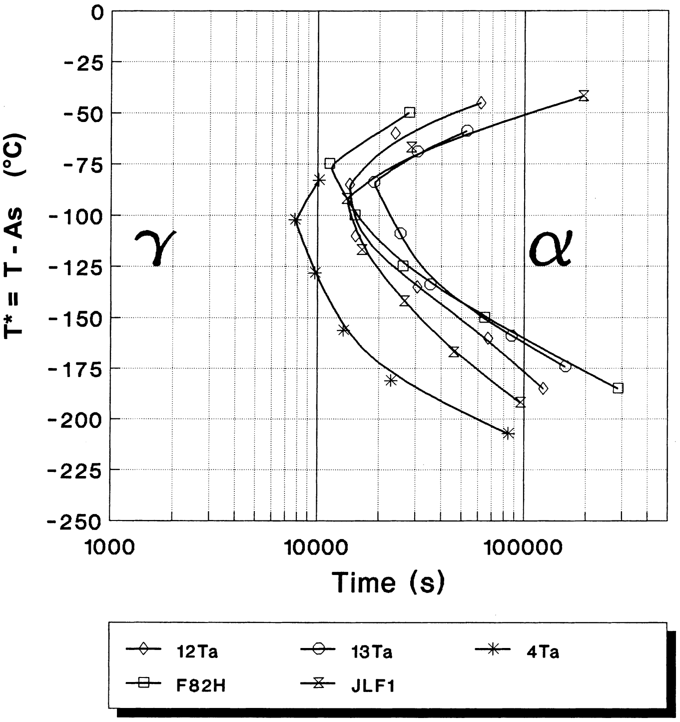

Fig. 4. TTT diagrams of different low activation martensitic steels showing time $t_{99\%}$ to complete transformation of austenite into ferrite. T* represents the shift of the temperature of isothermal transformation from As temperature (see Fig. 1).

Diagrams were established from $t_{1\%}$, $t_{50\%}$, $t_{99\%}$, which are the times to obtain 1, 50 and 99% of transformed austenite. TTT diagrams present the typical "C" curves (Fig. 4), already observed on conventional 9Cr–1Mo steels [5]. The "nose" of TTT curves, corresponding to the faster kinetics of the phase transformation, occurs at 700–725°C for alloys of 9Cr–0.8W type (high and low C, with and without Ta) and about 750–775°C for higher W and Cr containing steels. To compare the kinetics of different alloys, the $t_{99\%}$ curves have been represented using the parameter $T^* = T-$As corresponding to the difference between the isothermal transformation temperature and the As point. According to the representation shown in Fig. 4, in all the cases the faster kinetics occur at about 75–100°C down from As point. Transformation times are of the same order of magnitude for all materials, except for Cr-rich LA4Ta steel, where process seems to be faster; the slower reaction kinetic is found for LA13Ta (3%W).

The apparent activation energy of the isothermal transformation was estimated in the range 625–725°C for different fractions of transformed austenite, according to [11]. Estimated average values range from 150 (LA12LC) to 325 kJ/mole (F82H). These values are much higher than activation energies for interstitial atom (C and N) diffusion, but they are comparable to the activation energy for bulk diffusion of substitutional atoms like Fe, Cr, W, which ranges from 200 to 350 kJ/mole according to [12,13]. The higher values of activation energy are obtained for alloys displaying higher concentrations of W and Cr.

The microstructure of the ferritic matrix and in particular precipitated carbides of FeCrWVTa steels present similar characteristics as observed in conventional 9Cr–1Mo steels [5], that is a "perlitic" morphology above 725°C and "interphase" precipitation below 725°C. Nevertheless, F82H (7.5%Cr) displays a different morphology of precipitated carbides compared to 9–11%Cr steels.

4.2. *Effects of austenitisation and tempering treatments*

Effects of austenitisation heat-treatments have been examined on hardness and prior austenite grain size. They have been performed in the range 950–1150°C for 30 min.

For each material, austenitisation temperature has only a slight influence on the as-quenched martensite hardness as shown in Fig. 5. But, the hardness level of as-quenched martensite exhibit a linear relation with the (C + N) nominal concentration, which means that interstitial atoms in solid solution produce the main contribution to hardness compared to other alloying elements (Cr, W, V, Ta) and the morphological parameters as austenite grain size, length and width of martensite laths.

As shown in Fig. 6, Ta containing steels present more refined grain sizes for all the austenitisation temperatures, probably related to the pinning effect of undissolved Ta-rich carbonitrides. Nevertheless, for intermediate austenitisation temperatures as 1070–1100°C, a very heterogeneous grain size distribution was obtained as shown in Fig. 6(c), probably related to a non-homogeneous distribution of Ta-rich carbonitrides. In this case, the correlation of mechanical properties with the average grain size is meaningless, because coarse grains should impose their own behaviour, which will be detrimental especially for impact properties [14].

Recovery by tempering of the as-quenched martensite hardness is shown in Fig. 7 for F82H steel. The

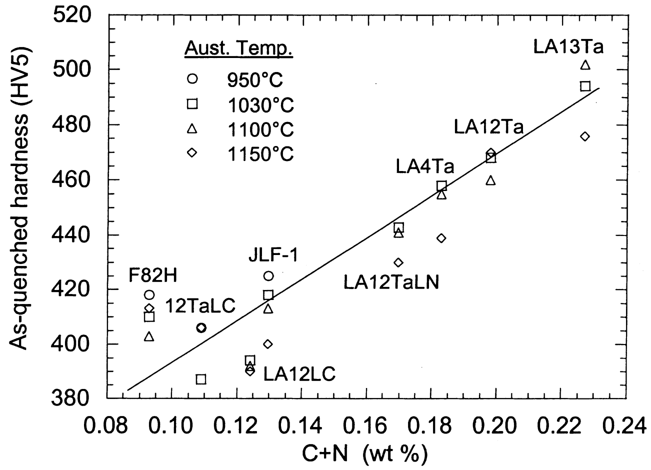

Fig. 5. As-quenched hardness measured after various austenitisation treatments, showing their linear relationship with (C + N) interstitial content.

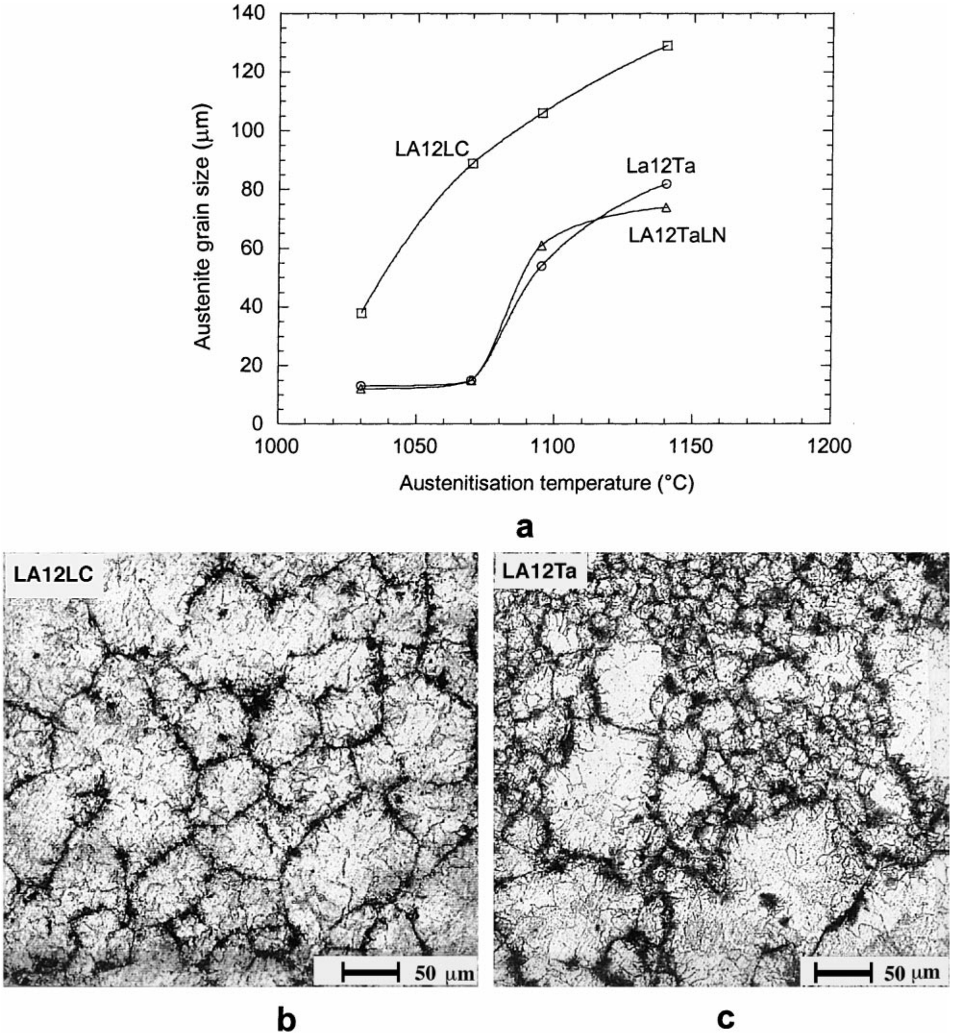

Fig. 6. Effect of austenitisation temperature on prior austenite grain size (a) for alloys with Ta (LA12Ta and LA12Ta LN) and without Ta (LA12LC). Grain structure obtained after austenitisation at 1070°C for 30 min showing homogeneous (b) and heterogeneous grain size distribution (c) for LA12LC and LA12Ta steels.

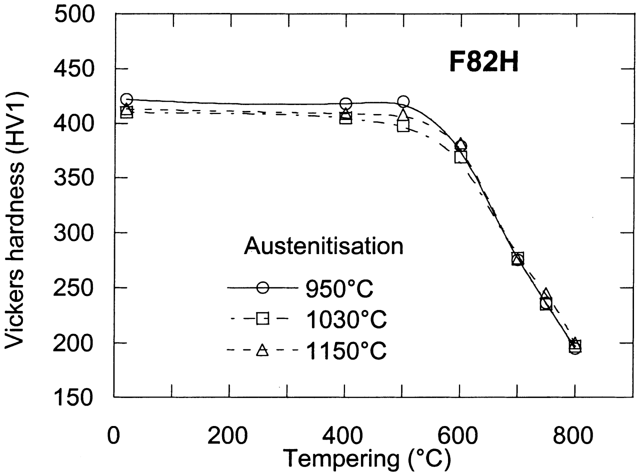

Fig. 7. Recovery of as-quenched hardness after isochronal tempering (1 h).

behaviour of all materials is quite similar and no sensitive effect of austenitisation temperature is observed. The isochronal curves display some trend to secondary hardening at 500°C, but of lower intensity as compared to 9Cr–1Mo conventional martensitic steels.

Tempering in the range 700–800°C induces a stable precipitation fraction of $M_{23}C_6$ carbides with a composition of about 55%Cr–30%Fe–12%W (in wt %).

4.3. Mechanical behaviour

F82H and JLF-1 steels were tested in the as-received N&T condition. LA experimental materials have been produced in N&T–CW condition, that is normalisation and tempering followed by 10% cold-working. To avoid heterogeneous grain size distribution, alloys were austenitised at 1030°C; depending on alloys, tempering was performed at 750–795°C to obtain the same hardness level before cold-working.

Tensile strength and ductility values of LA-materials and 9Cr–1Mo conventional steel are shown in Fig. 8(a). Compared to N&T specimens, higher values of UTS as well as 0.2% proof stress (up to 300 MPa at 20°C) were found for materials in N&T–CW condition, specially for W-rich, Cr-rich and high carbon containing alloys. The lowest values of tensile strength are found for low carbon N&T–CW LA-steels and are comparable to N&T large-scale heats for temperatures higher than 500°C. Experimental and industrial heats exhibit very similar ductility values as shown in Fig. 8(b).

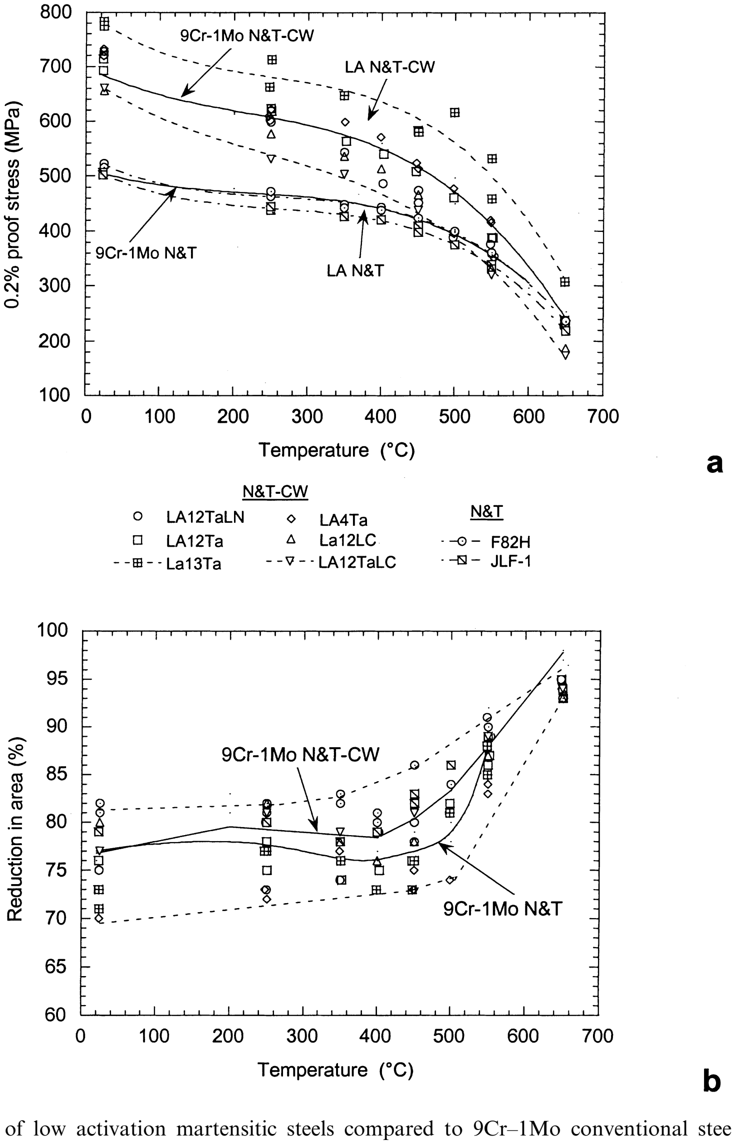

Fig. 8. Tensile properties of low activation martensitic steels compared to 9Cr–1Mo conventional steel in N&T and N&T–CW metallurgical conditions.

Table 3
Impact properties of low activation martensitic steels compared to 9Cr–1Mo conventional steel

Steel	DBTT(°C)	USE(J/cm^2)	Metallurgical condition
LA12Ta	−60	180	N&T–CW
LA12TaLN	−60	165	N&T–CW
LA12LC	−60	180	N&T–CW
LA4Ta	−70	155	N&T–CW
LA13Ta	−55	140	N&T–CW
9Cr–1Mo	−60	165	N&T–CW
F82H	−60	200	N&T
JLF-1	−70	180	N&T
9Cr–1Mo	−80	180	N&T

All materials exhibit also quite similar impact properties. DBTT ranges from −70°C to −55°C and values of the upper shelf energy (USE) from 140 to 200 J/cm^2. In contrast to tensile properties, impact behaviour seems to be less sensitive to the metallurgical condition of materials. Equivalent DBTT values were found for N&T and N&T–CW specimens, as shown in Table 3. The main difference comes from USE level, the lower ones are obtained for the stronger alloys.

Tensile as well as impact properties of LA-materials are equivalent to those of 9Cr–1Mo conventional steels. Their evolution under thermal ageing will depend on the initial metallurgical condition. A more stable behaviour and a better strength/ductility ratio is expected for N&T–CW specimens as already observed in thermal-aged conventional steels [15].

5. Conclusions

Effects of the chemical composition on austenitisation and tempering treatments, phase transformations and mechanical behaviour of low activation martensitic steels have been analysed. The results obtained allow a better understanding of the physical metallurgy of 7.5/11CrWVTa steels and enable to determine adequate metallurgical conditions to optimise their mechanical behaviour. In particular, to improve impact properties, austenitisation treatments need to be performed at temperatures lower than 1050°C to obtain a fine grain structure of austenite. On the other hand, tempering should be done at temperatures higher than 700°C to induce a stable carbide precipitation and to reach acceptable DBTT values.

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