Prediction of martensite start temperature of power plant steels

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Steels used in the construction of modern power plant contain relatively large concentrations of alloying elements. The martensite start temperature of such steels is important during fabrication, and can not be estimated using conventional empirical methods. It is demonstrated in the present paper that a recent theory due to Ghosh and Olson can be applied to predict both published and new experimental data on the martensite transformation temperatures of power plant steels. However, the method should not be used in circumstances where the steels contain δ ferrite or undissolved carbides before transformation.

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Introduction

It is planned that in future, power stations will be designed to operate with steam temperatures in excess of 600°C. The steels currently being developed to cope with these requirements contain a total solute concentration which is often in excess of 14 wt-%. The main solutes include strong carbide forming elements such as chromium and molybdenum, with the chromium also providing the necessary corrosion and oxidation resistance for prolonged elevated temperature service. The main alloys under consideration include numerous variants of the classical 12Cr–1Mo and 9Cr–1Mo steels.[1–3] These alloys have a high hardenability and a microstructure which is predominantly martensitic on cooling from the austenitisation temperature. Their martensite start M_s temperatures are therefore of considerable importance in deciding on the exact welding conditions necessary to avoid cracking.[1–3]

Martensite start temperatures are usually relatively easy to calculate using empirical equations[4–11] as long as the steels have a low alloy content. Even though empirical equations exist for high alloy steels, they are not sufficiently general and are known to provide inaccurate answers for the new power plant alloys, even when these alloys are fully austenitic (without δ ferrite or undissolved carbides).[12]

An alternative approach is to use thermodynamic theory,[13–15] which has the advantage that any solute combination can be considered provided the thermodynamic data are available. In the thermodynamic approach, martensite is said to be triggered when the chemical driving force for composition-invariant transformation of austenite to martensite of the same composition achieves some critical value at the M_s temperature

$$\Delta G^{\gamma\alpha'}\{M_s\} = \Delta G_C^{\gamma\alpha'} \qquad (1)$$

where $\Delta G^{\gamma\alpha'}\{T\}$ is the free energy change accompanying the transformation of austenite to martensite of the same composition at a temperature T. This differs from the corresponding term $\Delta G^{\gamma\alpha}$ for the transformation of austenite to ferrite of the same composition because the latter does not allow for the Zener ordering of the carbon atoms.[16,17] The term $\Delta G_C^{\gamma\alpha'}$ is the critical value of the driving force needed to trigger martensitic transformation. The method for calculating the M_s temperature is illustrated in Fig. 1. This method has been used successfully for low alloy steels where it has been possible to rationalise experimental data by allowing $\Delta G_C^{\gamma\alpha'}$ to assume either a constant value of about $-1100\ \mathrm{J\ mol^{-1}}$ or by allowing it to vary slightly with the carbon concentration, the exact variation being defined empirically.[14,15]

Neither of these methods work well when applied to high alloy steels. The purpose of the present work was to see whether a new model developed by Ghosh and Olson,[18,19] which takes into consideration the strengthening of austenite caused by solute additions, can be applied to the calculation of the M_s temperatures of highly alloyed power plant steels. The model is tested against published data as well as new experimental measurements.

Ghosh and Olson model

The Olson and Cohen model[20] for the nucleation of martensite relies on barrier-less nucleation, in which there are no heterophase fluctuations as in conventional nucleation theory, but the nucleation event is defined by the faulting caused by the dissociation of a pre-existing array of dislocations. Consequently, the activation energy for nucleation is that associated with the motion of the partial dislocations. The dislocations migrate against a frictional stress τ_O which consists of the sum of a thermal τ_{th}, and athermal τ_μ term. The dislocations must therefore experience a force per unit length which is given by

$$(\tau_\mu + \tau_{th})bn$$

before they can migrate. In this expression, b is the magnitude of the Burgers vector and n is the number of planes over which the faulting occurs (i.e. the number of dislocations in the array). This is the force which opposes the motion of the array. However, when transformation is favoured, the faults created by the dissociation are energetically favoured, i.e. the fault energy per unit area γ_f becomes negative. This gives total change in energy due to faulting as

$$\gamma_f = n\rho_A(\Delta G^{\gamma\alpha'} + G_s) + 2\sigma \qquad (2)$$

where ρ_A is the density of atoms in the fault plane, G_s is the strain caused by the embryo, and σ is the interface energy per unit area of embryo; the energies G are expressed here in Joules per unit volume.

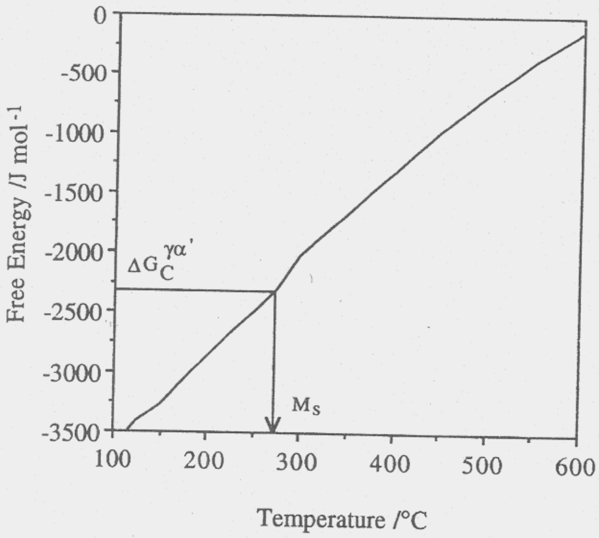
The embryo becomes unstable (i.e. becomes a nucleus) when the force on the dislocations due to the negative fault energy overcomes the frictional force

$$-\gamma_f = (\tau_\mu + \tau_{th})bn \qquad (3)$$

It follows from the previous equations that

$$n\rho_A(\Delta G^{\gamma\alpha'} + G_s) + 2\sigma = -(\tau_\mu + \tau_{th})bn \qquad (4)$$

If $\Delta G^{\gamma\alpha'}$ is now set equal to $\Delta G_C^{\gamma\alpha'}$, and it is assumed that the τ_{th} can be neglected due to the high temperatures



1 **Calculation of martensite start temperature as point where chemical driving force for transformation of austenite without composition change achieves critical value**

involved, then

$$\Delta G_C^{\gamma\alpha'} = -\rho_A^{-1}(b\tau_\mu - 2\sigma) - G_s \quad . \ . \ . \ . \ . \ . \ . \ . \ . \quad (5)$$

which has the form

$$\Delta G_C^{\gamma\alpha'} = K_1 + K_\mu \phi\{c\} \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad (6)$$

where K_1 includes the combined effects of the interfacial and strain energy terms, and K_μ is a coefficient, which when multiplied by the function ϕ of composition c incorporates the effect of solid solution strengthening by alloying additions on τ_μ.

This is an important equation because it explicitly defines the critical driving force $\Delta G_C^{\gamma\alpha'}$ in terms of solute concentration. Ghosh and Olson used solid solution theory to obtain the form of the relationship, and experimental data to obtain the coefficients K_μ

$$\begin{aligned} -\Delta G_C^{\gamma\alpha'} = K_1 &+ 4009c_C^{0\cdot5} + 1879c_{Si}^{0\cdot5} + 1980c_{Mn}^{0\cdot5} + 172c_{Ni}^{0\cdot5} \\ &+ 1418c_{Mo}^{0\cdot5} + 1868c_{Cr}^{0\cdot5} + 1618c_V^{0\cdot5} + 752c_{Cu}^{0\cdot5} \\ &+ 714c_W^{0\cdot5} + 1653c_{Nb}^{0\cdot5} + 3097c_N^{0\cdot5} - 352c_{Co}^{0\cdot5} \quad (7) \end{aligned}$$

The coefficients were obtained by establishing the $c^{0\cdot5}$ dependence and fitting over a wide range of compositions: the maximum concentrations were approximately 2 wt-% for carbon and nitrogen, 0·9 wt-% vanadium and about 2–28 wt-% for all the other alloying elements.[18,19,21] Ghosh and Olson quoted a value of $K_1 = 1010\ \mathrm{J\ mol^{-1}}$. It was intended in the present work to use this equation to attempt to predict the martensite start temperatures of power plant alloys.

Calculation of free energy change

The free energy change $\Delta G^{\gamma\alpha}$ for the transformation of austenite to ferrite of the same composition can be estimated as a function of temperature using standard thermodynamic data and appropriate software to interpret these data. The database used here is SGTE (Scientific Group Thermodata Europe), which is an assessed and reliable database. The computer program used to access and interpret these data was Mtdata, a package developed by the National Physical Laboratory, UK. The combination of data and software can enable the free energy changes to be calculated routinely for multicomponent steels.

However, to calculate $\Delta G^{\gamma\alpha'}$ also requires an estimation of the Zener ordering energy, which arises because carbon atoms in ferrite can in some circumstances order on one of the three available sublattices of octahedral interstitial sites, thereby changing the symmetry of the lattice from bcc to bct.

The ordering temperature T_C is a function of the carbon concentration[17]

$$T_C\{K\} = \frac{T(1-x)}{28080x} \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad (8)$$

where x is the mole fraction of carbon. If the M_s temperature exceeds T_C then the martensite is bcc, but when it is below T_C, the ordering energy G_{Zener} is a complicated function of temperature and carbon concentration, and was calculated as in Ref. 17. The required free energy is then given by

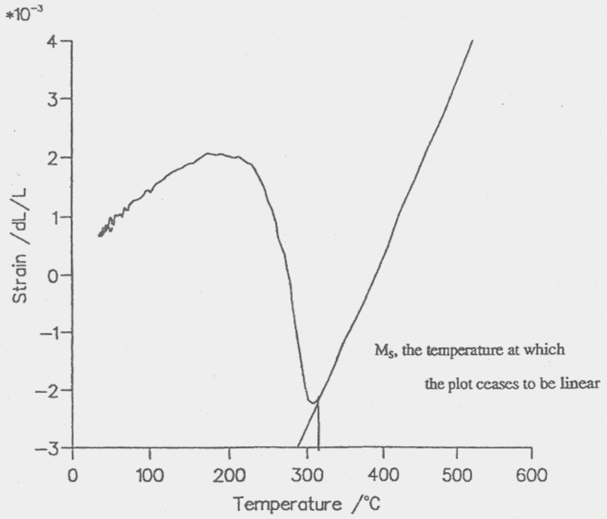
$$\Delta G^{\gamma\alpha'} = \Delta G^{\gamma\alpha} + G_{Zener} \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad (9)$$

Experimental technique

The chemical compositions of the alloys studied are given in Table 1. The samples consisted of wrought steels and those produced by welding. The former were supplied by Rolls-Royce Industrial Power Group and the latter by Oerlikon Welding Limited. The welded samples were machined from manual metal arc welds which were prepared to ISO2560 geometry, which ensures minimal dilution so that all-weld metal samples can be obtained, and the quoted compositions correspond to these all-weld metal samples.

Table 1 Composition of experimental samples, wt-%

	C	Si	Mn	Cr	Mo	Ni	Co	Cu	N	Nb	V	W
Wrought samples												
B158	0·20	0·084	0·64	2·12	0·83	0·76	0·013	0·045	0·006	0·020	0·32	0·63
4HSG	0·29	0·22	0·85	0·97	0·65	0·73	0·021	0·16	0·012	0·017	0·26	0·011
HYE	0·25	0·34	0·28	1·60	0·46	3·51	0·069	0·13	0·009	0·020	0·13	0·017
97	0·14	0·20	0·52	0·30	0·56	0·084	0·021	0·088	0·011	0·010	0·23	0·007
P91	0·093	0·41	0·49	9·08	0·92	0·23	0·012	0·12	0·035	0	0·25	0
Steel F	0·13	0·19	0·55	10·2	1·51	0·62	0·10	0·050	0·060	0	0·21	0
ADQ	0·11	0·026	0·44	2·01	0·94	0·043	0·008	0·032	0·005	0·022	0·008	0·009
Welded samples												
–	0·099	0·17	1·01	9·30	1·00	0·08	…	0·0180	0·0539	0·0460	0·20	…
1Ni	0·093	0·16	1·03	9·08	0·98	0·98	…	0·0180	0·0515	0·0430	0·19	…
2Ni	0·101	0·17	1·02	9·12	1·00	1·92	…	0·0190	0·0494	0·0470	0·19	…
3Ni	0·095	0·16	1·02	9·17	0·96	3·01	…	0·0180	0·0489	0·0450	0·19	…
1W	0·095	0·18	1·04	9·35	1·00	0·08	…	0·0170	0·0544	0·0510	0·19	1·03
2W	0·096	0·20	0·99	9·25	0·91	0·08	…	0·0180	0·0526	0·0530	0·19	1·92
3W	0·094	0·20	1·03	9·26	0·84	0·08	…	0·0190	0·0537	0·0580	0·19	2·99
1Ni1W	0·097	0·18	1·00	9·10	0·96	0·93	…	0·0170	0·0529	0·0460	0·19	0·98



2 Determination of martensite start temperature from recorded strain versus temperature curve obtained using thermomechanical simulator

The alloys provided were machined into cylindrical samples 8 mm in diameter and 12 mm in length. Transformation experiments were performed using a Thermecmaster-Z thermomechanical simulator, which is equipped to enable the simultaneous recording of the diametric and longitudinal length changes (strain), in addition to time, temperature, and load data. The specimen was in each instance heated using a radio frequency coil and the temperature was measured with a Pt/Pt–10Rh thermocouple spot welded to the sample.

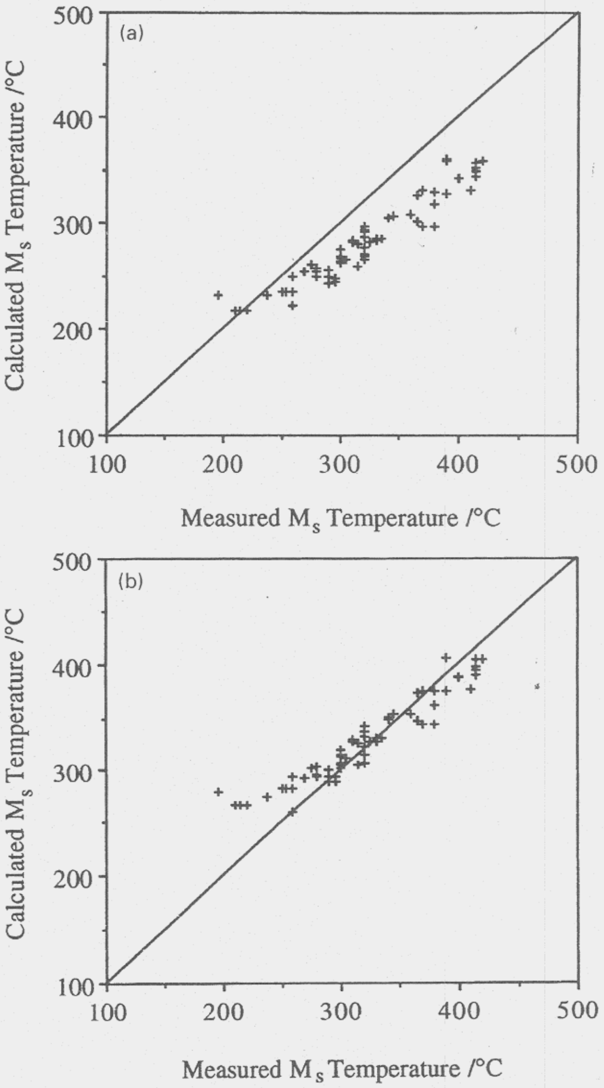
The martensite start temperature was obtained by heating the sample to 1100°C for 600 s in the simulator, followed by quenching at about 50 K s^{-1} using helium gas. On plotting strain versus temperature, the M_s temperature could easily be found at the point where the curve deviated from the straight line corresponding to the thermal contraction of austenite. This is illustrated for a typical instance in Fig. 2.

It has been verified, using a multicomponent, multiphase diagram calculation method,[22] that the austenitisation temperature of 1100°C is sufficiently high to be in the single phase austenite region. Thus, all the carbides should be dissolved. These calculations were carried out allowing the austenite, ferrite, cementite, M_2C, $M_{23}C_6$, M_6C, M_7C_3, M_3C_2, σ, and Laves phases to exist. None of these were found to be stable precipitates at 1100°C, so this was the austenitisation temperature selected.

Comparison between calculated and measured M_s

PUBLISHED DATA

An initial comparison was made of the calculated M_s temperatures against the vast range of low alloy steels studied by Steven and Haynes[4] and some other high alloy samples (12Cr–Mo–V and 9Cr–1Mo) investigated elsewhere.[12] Figure 3*a* shows the results; the theory tends to systematically underestimate the transformation temperature, indicating that the value of K_1 is probably too large. The value of K_1 was therefore varied, and 683 J mol^{-1} was found to give optimum agreement, as indicated in Fig. 3*b*. The accuracy for the lowest of M_s temperatures is relatively poor, but this can not be attributed to equation (7) since the concentration range covered by the relation is greater than utilised in the present work. This modified value was used in all subsequent calculations.

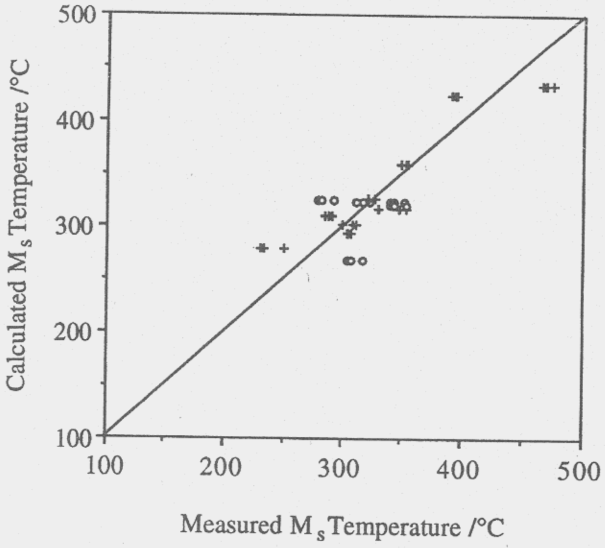


3 Calculated M_s temperatures versus those measured (published data): line has unit slope and zero intercept, so that any point on line indicates perfect agreement between experiment and theory (analysis uses equation due to Ghosh and Olson for $\Delta G_{\mathrm{C}}^{\gamma\alpha'}$, with *a* $K_1 = 1010$ J mol^{-1} and *b* modified value of $K_1 =$ 683 J mol^{-1})

NEW EXPERIMENTAL DATA

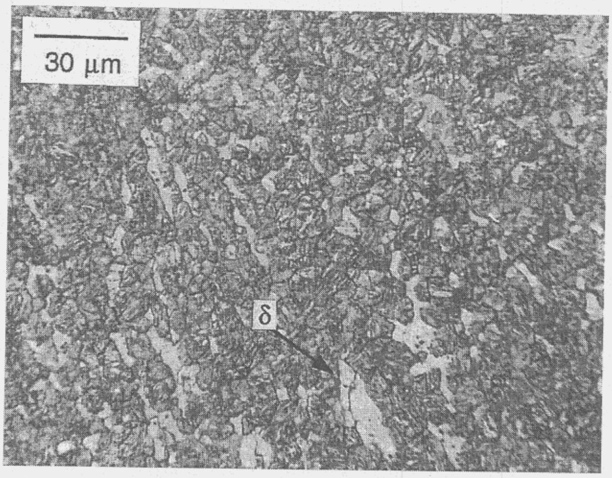
Figure 4 shows a comparison of calculated M_s temperatures of the alloys listed in Table 1, versus their measured transformation temperatures. There is in general good agreement, but the observed scatter is greater than in Fig. 3*b*. The reasons are not clear, but there are some special difficulties in the tungsten containing alloys.

The tungsten containing 9%Cr alloys are presented in more detail in Fig. 5; it appears that large concentrations of tungsten lead to poor predictability. Further investigation revealed that the 1%W alloy does not become fully austenitic at 1100°C (or at higher austenitisation temperatures); metallography revealed the presence of δ ferrite (Fig. 6), consistent with the fact that the hardness of the 3%W alloy was also much lower than that of the other tungsten containing alloys (340 HV10 compared with 400 HV10). It is therefore not surprising that the calculated martensite start temperature does not agree with that measured. In fact, thermodynamic calculations[22] revealed that at equilibrium, all of the alloys containing 1 wt-% or more of tungsten should contain some ferrite at 1100°C. The data from all such alloys have been identified in Fig. 4,



circles identify alloys which are likely to contain δ ferrite after heat treatment at 1100°C

4 Calculated M_s temperatures versus those measured for experimental alloys listed in Table 1: line has unit slope and zero intercept, so that any point on line indicates perfect agreement between experiment and theory (analysis uses equation due to Ghosh and Olson for $\Delta G_{C}^{\gamma\alpha'}$, with $K_1 = 683$ J mol^{-1})



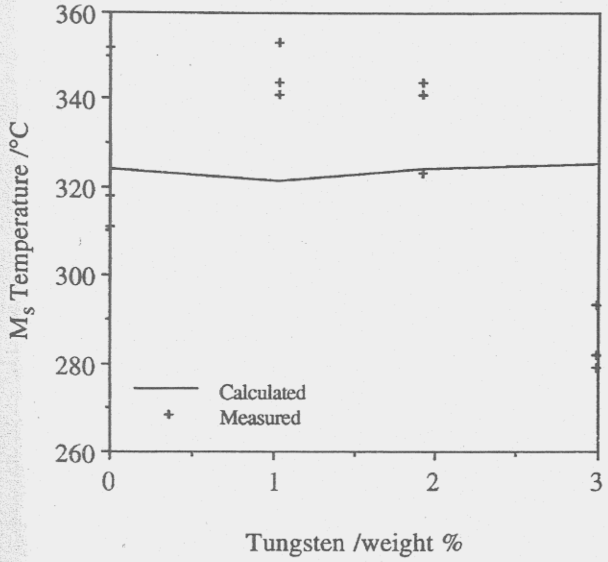
6 Micrograph showing presence of δ ferrite in 3 wt-% tungsten containing alloy (Table 1) after quenching from 1100°C (optical)

and might explain the additional scatter apparent in Fig. 4 when compared with Fig. 3*b*.

The Ghosh and Olson method was intended to apply to fully austenitic alloys, and relies on the availability of accurate thermodynamic data. Care must therefore be exercised in the application of the method to power plant steels in particular.

Conclusions

In the Ghosh and Olson method for the calculation of the martensite start temperature, the critical value of the driving force needed to trigger martensitic transformation is a function of the solid solution hardening ability of alloying elements. It has been demonstrated here that the method can be used reliably to predict the martensite start temperatures of a wide range of power plant steels, including those which are rich in alloying elements. The addition of large concentrations of tungsten (3 wt-%) to the 9Cr–1Mo steels makes it impossible to fully austenitise the alloy. This makes it difficult to calculate the M_s temperature of the partially austenitic sample. The effect of δ ferrite and of undissolved carbides on the M_s temperature requires further investigation.



5 Calculated M_s temperatures versus those measured for tungsten containing experimental alloys listed in Table 1

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