The electronic structure of the alloying element and the stability of the gamma phase in iron alloys

Recently, Pettifor [1] has made a density of states calculation for fcc, hcp and bcc lattices, at constant volume per atom, based on the "hybrid-nearly free electron-tightly bound" model. The bands were filled with electrons and the total electron energy for three structures obtained for any number N_P of (s + p) electrons. The calculations indicate that the bcc phase is more stable at absolute zero than the fcc for $7 > N_P > 3$. If coupling via the hybridization to the conduction block is neglected, the energy of the pure d-band is lower for bcc than for fcc for $6 > N_P > 1$. The success of Pettifor [1] in accounting for the observed structure of transition metals of the third, fourth and fifth periods using this model has raised interest in the use of electron concentration as a criterion for predicting the stability of the gamma phase in iron alloys.

In Table I the value of N (which is the sum of the d electrons in unfilled d bands and s and p electrons in the valence band) for various elements is compared with their effect on the gamma field in iron alloys. It appears that the elements that decrease the stability of the gamma phase (gamma-loop formers) have values for N ranging from two to six. The gamma stabilizers are elements that have values for N from 7 to 10 or 1. Interstitial solutes, like carbon and nitrogen, that stabilize gamma iron due to geometric factors, are not included in the table. For plutonium, which has an unfilled f band in addition to an unfilled d band, N is equal to the total number of electrons in unfilled bands and valence band. The general validity of this empirical correlation makes it useful for assessing the effect of other solutes, alone or in combination, on the stability of the gamma phase in iron alloys. Properties like hardenability of steels are related to the driving force for gamma → alpha transition, and can be qualitatively assessed from the electronic structure of the alloying elements.

From a fundamental viewpoint, the fcc structure is expected to be more stable than the bcc structure at low temperatures because of the closer packing of atoms; a value of approximately 200 cal g at.$^{-1}$ can be estimated for the difference in energies using an elastic model. The low temperature stability of bcc iron is due to magnetic ordering, the energy and entropy of which are given by,

$$\Delta H_\mathrm{m} = \int_0^T C_{\mathrm{P_m}}\,\mathrm{d}T = ZkNS^2 \qquad (1)$$

$$\Delta S_\mathrm{m} = \int_0^T \frac{C_{\mathrm{P_m}}}{T}\,\mathrm{d}T = R\ln(2S+1) \qquad (2)$$

where Z is the co-ordination number, N is Avagadro's number, S is the spin, k is the coupling factor which depends on structure and composition, and $C_{\mathrm{P_m}}$ is the magnetic contribution to the heat capacity. Heat capacity measurements on alpha iron listed by Hultgren *et al.* [2] indicate a value of 1925 cal g at.$^{-1}$ for ΔH_m and 2.05 cal deg^{-1} g at.$^{-1}$ for ΔS_m. These values are related to the transition temperature (Curie point) by the relation,

TABLE I Relationship between the electronic structure of the alloying element and the stability of the gamma phase

Element	N	Phase stabilized
Al	3	bcc
As	5	bcc
Be	2	bcc
Cr	6	bcc
Ge	4	bcc
Hf	4	bcc
Mo	6	bcc
Nb	5	bcc
P	5	bcc
Sb	5	bcc
Si	4	bcc
Sn	4	bcc
Ta	5	bcc
Ti	4	bcc
V	5	bcc
W	6	bcc
Zn	2	bcc
Zr	4	bcc
Au	1	fcc
Co	9	fcc
Cu	1	fcc
Mn	7	fcc
Ni	10	fcc
Os	8	fcc
Pd	10	fcc
Pt	10	fcc
Pu	10	fcc
Rh	9	fcc
Ru	8	fcc
Tc	7	fcc

$$\frac{\Delta H_{\mathrm{m}}}{\Delta S_{\mathrm{m}}} = aT_{\mathrm{t}} \tag{3}$$

where a is a constant depending on the shape of the $C_{\mathrm{P_m}}$ versus T curve, and has a value 0.8 to 0.9 for second order transitions [3]. The magnetic disorder temperature for gamma iron (Néel temperature) has been found to be 60 K from measurements on metastable electrodeposited thin films [4]. The entropy of magnetic disordering is the same for bcc and fcc phases, since it is only a function of the number of electrons involved (Equation 2). The heat of magnetic disordering for fcc phase can, therefore, be estimated using Equation 3 as 110 cal g at.$^{-1}$. The less-dense packing of atoms would correspond to a lower frequency of atomic vibration and result in slightly higher entropy for bcc phase than for the fcc phase. The free energy difference between the alpha and the gamma phases according to this scheme is plotted as a function of temperature in Fig. 1. The model differs from Zener's "two-gamma-model" [5], where the magnetic moment on any fcc atom can take two values with two states having different energies.

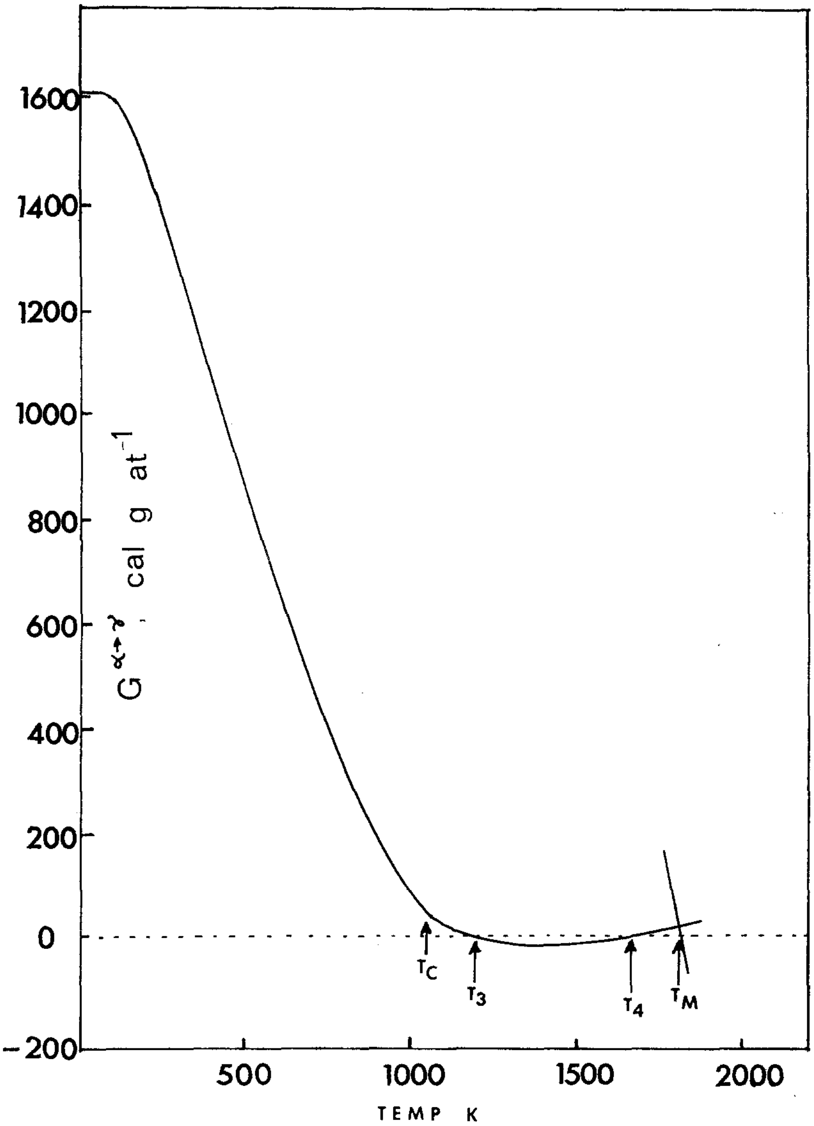

Figure 1 The variation of the difference in the calculated free energy of pure alpha and gamma iron with temperature.

Alloying elements can have three effects on the relative stability of the gamma phase:

(i) Alter the lattice and electronic contributions to the heat capacity;

(ii) Alter the magnetic properties (i.e. values of k and a) of the bcc and fcc phases. Few heat capacity data on iron alloys are available for assessing systematic variation of these parameters with electronic configuration. Information on atomic moments (μ_B) in transition metal alloys [6] indicates that the electron population in pure iron corresponds approximately to the maximum spin, so that significant increase in spin cannot be obtained by alloying;

(iii) If the excess free energy of solution of the alloying element in the bcc and fcc iron is different, the alloying element will stabilize one phase relative to the other. The difference in the excess free energy of solution is caused mainly by difference in the free energy of the pure alloying element in bcc and fcc structures.

Sinha *et al.* [7] have evaluated the difference in the partial free energies of the alloying elements in alpha and gamma phases from an approximate analysis of phase equilibria, and have found that the values correlate with differences in lattice stabilities of pure alloying elements in fcc and bcc forms obtained from Kaufman's data. This indicates that the non-magnetic solution effect may be the predominant term accounting for the close similarity between Pettifor's relation of the phase stability of the pure transition metals to electronic structure, and the relationship between the relative stability of the gamma phase and electron concentration (N) obtained in this study.

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