A thermo-mechanical correlation with driving forces for hcp martensite and twin formations in the Fe–Mn–C system exhibiting multicomposition sets

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Abstract
The thermodynamic properties of the Fe–Mn–C system were investigated by using an analytical model constructed by a CALPHAD approach. The stacking fault energy (SFE) of the fcc structure with respect to the hcp phase was always constant at $T_0$, independent of the composition and temperature when other related parameters were assumed to be constant. Experimental limits for the thermal hcp formation and the mechanical (deformation-induced) hcp formation were separated by the SFE at $T_0$. The driving force for the fcc to hcp transition, defined as a dimensionless value $-dG_m/(RT)$, was determined in the presence of Fe-rich and Mn-rich composition sets in each phase. Carbon tended to partition to the Mn-rich phase rather than to the Fe-rich phase for the compositions studied. The results obtained revealed a thermo-mechanical correlation with empirical yield strength, maximum true stress and maximum true strain. The proportionality between thermodynamics and mechanical properties is discussed.

Keywords: stacking fault energy, high manganese steel, TWIP, TRIP, shape memory alloys

1. Introduction
Fe–Mn base austenitic alloys have been the subject of various studies because of their superior mechanical properties useful to many industrial applications [9, 21, 22, 27, 39, 40]. These alloys exhibit considerable strength and ductility depending on deformation modes that the alloys undergo. The high work hardening rate of these alloys is related to the formation of deformation twins in the fcc matrix as well as bct ($\alpha'$) and hcp ($\varepsilon$) martensitic phases. It has been discussed that the stacking fault energy (SFE) may indicate the magnitude of dislocation dissociations into Shockley partials, affecting the subsequent work hardening rate. Alloys with low SFE tend to form mechanical (deformation-induced) hcp martensite and those with high SFE exhibit only dislocation glide; mechanical twinning occurs for intermediate SFE values [3, 32]. A mechanical correlation with the thermodynamic property can be rationalized as a stacking fault comprises an embryo of hcp stacking or a twin. Correlations of the SFE values with deformation modes, i.e. the formation of hcp martensite, twin or only dislocation glide, have been extensively reported [2, 3, 14, 19, 32, 33]. The SFE values may not be the sole parameter responsible for such deformation behaviors [6].

In this work, an analytical model for the hcp phase in the Fe–Mn–C system constructed by a calculation
of phase diagrams (CALPHAD) technique [26] was used to investigate correlations between mechanical and thermodynamic properties. The SFE of the fcc phase with respect to the hcp phase in the Fe–Mn–C system was evaluated with an emphasis on the alloys’ mechanical properties. Thermo-Calc software (version S) [4] was used for the calculations with the proposed thermodynamic parameters. Peculiarities associated with other related thermodynamic properties, such as $T_c$ and driving force for the hcp transformation, were discussed along with the mechanical properties of alloys with different compositions.

2. Calculation method

2.1. Gibbs free energy of the hcp and fcc phases in the Fe–Mn system

Only the fcc and hcp phases were considered in this study. Thermodynamic parameters for the hcp phase were taken from [26] and those for the fcc phase were adopted from the work of Huang [18], where the stable phases in the Fe–Mn system are well assessed. The lattice stability values of the hcp and fcc phases of Fe and Mn are taken from Scientific Group Thermodata Europe (SGTE) [11]. Both phases are treated as solutions with random mixing in two sublattices, i.e. $(\text{Fe, Mn})_1(\text{Va})_1$ for fcc and $(\text{Fe, Mn})_1(\text{Va})_{0.5}$ for hcp, where $\text{Va}$ is the vacancy. The molar Gibbs energy of phase $\phi$ (= fcc or hcp) is expressed by

$$G_m^\phi = \sum_{i=0}^{6} x_i \phi \rho_i G_i^{\phi} + x_i \phi \sum_{i=0}^{6} x_i \phi \ln x_i \phi + x_i \phi \ln x_i \phi + \beta T \times m \ln x_i \phi + \text{RT} \times m \ln x_i \phi,$$

where $x$ is the mole fraction of a component, $\phi$ is the lattice stability of the phase of element $x$, $R$ is the gas constant and $T$ is the temperature. The excess term is described by the Redlich–Kister polynomial [31]

$$\chi_{m}^{\phi} = x_F^{\phi} \chi_{c}^{\phi} + x_M^{\phi} \chi_{m}^{\phi} + \sum_{i=0}^{6} x_i \phi \ln x_i \phi + x_i \phi \ln x_i \phi (\Delta L_m^{\phi},)$$

$$L_m^{\phi} = \sum_{i=0}^{6} x_i \phi \ln x_i \phi + x_i \phi \ln x_i \phi \Delta L_m^{\phi},$$

The interaction parameter $L$ in equation (2) is temperature dependent:

$$\Sigma_{i=0}^{6} x_i \phi \ln x_i \phi = a^{\phi} + b^{\phi} T + c^{\phi} T \ln T + \ldots ,$$

where $a$, $b$, $c$, . . . are the parameters determined in the previous work [26]. The magnetic order–disorder transition modifies the Gibbs energy of a phase and thus the relative stability of the phases. By practically simplifying Inden’s model [20], Hillert and Jarl [16] described the magnetic contribution to the Gibbs energy as

$$\chi_{m}^{\phi} = \beta T \ln (\beta^{\phi} + 1) g (\tau),$$

where $\beta$ is an average magnetic moment per atom in Bohr magnetons. The last term is a function of $\tau (= T / T_c)$, with $T_c$ being the magnetic transition temperature. Details of the magnetic contribution to the Fe–Mn system are described elsewhere [26].

2.2. Stacking fault energy

Following the model of Olson and Cohen [28], the SFE is calculated as

$$\text{SFE (mJ m}^{-2}) = n \rho (\Delta G_{\text{fcc→hcp}} + \Delta G_{\text{strain}}) + n \sigma_n$$

where $n$ is the number of planes (assumed to be 2), $\rho$ is the atomic density of the $\{111\}$ planes, $\Delta G_{\text{fcc→hcp}}$ is the Gibbs free energy difference between the hcp and fcc phases, $\Delta G_{\text{strain}}$ is the strain energy and $\sigma$ is the energy at the hcp/fcc interface. The atomic density $\rho$ is of the order of $10^{-2} \text{m}^2$ [3, 24]. According to Cotes et al [10], $\Delta G_{\text{strain}}$ exhibits minimal composition dependence for 0–28 wt% Mn and it was therefore assumed to be $37 \text{J mol}^{-1}$ in this study; $\sigma = 0.016 \text{J m}^{-2}$ was assumed following previous work [26].

3. Results

3.1. Evolution of stacking fault energy

Figure 1 shows a variation of SFE with respect to Mn and C contents along with experimental data [29, 41, 42]. The SFE values decrease at small Mn contents and increase with higher amounts of Mn, indicating the presence of an SFE minimum in the system. A carbon addition moves the minimum to the Mn-richer side, which modifies a trend in the SFE evolution along with experimental data [29, 41, 42]. The SFE values decrease at small Mn contents and increase with higher amounts of Mn, indicating the presence of an SFE minimum in the system. A carbon addition moves the minimum to the Mn-richer side, which modifies a trend in the SFE evolution along with experimental data [29, 41, 42]. The SFE values decrease at small Mn contents and increase with higher amounts of Mn, indicating the presence of an SFE minimum in the system. A carbon addition moves the minimum to the Mn-richer side, which modifies a trend in the SFE evolution along with experimental data [29, 41, 42]. The SFE values decrease at small Mn contents and increase with higher amounts of Mn, indicating the presence of an SFE minimum in the system. A carbon addition moves the minimum to the Mn-richer side, which modifies a trend in the SFE evolution along with experimental data [29, 41, 42]. The SFE values decrease at small Mn contents and increase with higher amounts of Mn, indicating the presence of an SFE minimum in the system. A carbon addition moves the minimum to the Mn-richer side, which modifies a trend in the SFE evolution along with experimental data [29, 41, 42].
3.2. Effect of grain sizes and magnetic transition on SFE

The SFE is generally measured by taking a separation of partial dislocation nodes, which is inversely proportional to the SFE [35]. Small impurities may affect SFE to some extent [30]. If one assumes that carbon and other elements or impurities are pinned at grain boundaries during grain growth, grain sizes of austenite may influence the SFE as the local lattice concentration is also affected. \( T_{\text{Néel}} \) of the bulk fcc phase is also influenced by the grain size. If \( T_{\text{Néel}} \) of austenite decreases with increasing austenite grain size, the Gibbs free energy of the fcc phase with respect to the hcp phase increases, consequently reducing the SFE. However, such a grain boundary effect must be very subtle, especially for decent grain sizes.

The magnetic transition temperature for the fcc solution in Fe–Mn is composition dependent [3, 8, 18, 23, 45], and can be expressed as

\[
T_{c\phi} = T_{c\phi}^0 (1 - x_{\text{Mn}}) + \Delta T_{c\phi}^0 (1 - x_{\text{Mn}}) x_{\text{Mn}},
\]

where \( T_{c\phi} \) is the magnetic transition temperature of the phase \( \phi \) in a Fe–Mn solution, \( T_{c\phi}^0 \) is the magnetic transition point of the phase \( \phi \) in pure Fe and \( \Delta T_{c\phi}^0 \) is the excess temperature term from the interaction between Fe and Mn. Further details can be found in [26]. The calculated \( T_{\text{Néel}} \) values are shown in figure 2. Mn increases the critical temperature for magnetic transition, while C has an opposite effect. The C effect on \( T_{\text{Néel}} \) is relatively small compared to that on \( T_0 \). Below \( T_0 \), hcp martensite can transform from the fcc matrix on cooling, which would not occur above \( T_0 \) where formation of hcp martensite is only possible by mechanical deformation. Figure 2 indicates separations between magnetically ordered or disordered phases, above \( T_0 \) or below it. The addition of carbon effectively suppresses the thermal formation of hcp martensite while it stabilizes the paramagnetic fcc phase. The heat evolved from the application of external stress (e.g. rolling) moves the system into a different regime in figure 2. For example, an Fe–25Mn alloy is located in the ‘antiferromagnetic fcc+thermal hcp’ region at room temperature, but it moves into a region where thermal hcp is suppressed and the mechanical hcp formation is possible. Furthermore, the fcc phase is magnetically disordered in this region, increasing the relative stability of the hcp phase.

3.3. SFE along \( T_0 \) temperature

Figure 3 shows iso-SFE contours versus Mn and C concentrations in the Fe–Mn–C system. The SFE along \( T_0 \) never crosses the iso-SFE contours and is always constant. When the Gibbs free energy of the hcp phase is equal to that of the fcc phase, Olson and Cohen’s equation suggests a constant SFE by assuming other parameters to be constant. The constant SFE along \( T_0 \), determined as 32.7 mJ m\(^{-2}\), is independent of the composition and temperature studied as long as changes in the atomic density, strain energy and surface energy are negligible.

The calculated \( T_0 \) values are plotted together with experimental \( M_s \) (hcp martensite start) and \( A_s \) (austenite start) temperatures in figure 4 [1, 5, 9, 12, 13, 15, 21, 32, 37, 38, 39, 40]. Thermodynamic parameters to calculate \( T_0 \) were adopted from [26] where the parameters were optimized over \( T_0 \) temperatures determined by averaging the experimental \( M_s \) and \( A_s \) temperatures. Note that some data points in figure 4 were reported independently rather than as \( M_s - A_s \) pairs. Because \( M_s \) is always located below \( T_0 \), \( M_s \) is always located at lower Mn than the Mn concentration at \( T_0 \). If one assumes that \( M_s \) is located about 50°C below \( T_0 \), then the Mn concentration gap between \( M_s \) and \( T_0 \) varies depending on the Mn content in the Fe–Mn system. \( T_0 \) drops more rapidly below \( T_{\text{Néel}} \) as the fcc
The driving force for the transformation to the hcp phase

The driving force for the diffusionless transformation, determined at $M_s$ and $A_s$, is not constant in the Fe–Mn system [26]. The driving force for the martensitic transition at $M_s$ decreases with decreasing transformation temperature while that for the reverse transformation at $A_s$ increases with decreasing transition temperature. Less undercooling may be required for an hcp martensitic transition from the fcc phase at high Mn content, while the hcp to fcc transition shows the opposite trend. $M_s$ temperatures are thus located closer to $T_0$ temperatures at Mn contents greater than the $T_0/T_{N\text{ecl}}$ intersection, whereas $A_s$ temperatures are further away from $T_0$ temperature at higher Mn, depending on the locations relative to the Mn concentration where a magnetic transition occurs. As a result, the driving force for the fcc to hcp transition tends to increase with temperature (i.e. lower Mn), while that for the reverse transition tends to decrease with temperature (lower Mn). A sufficient amount of the positive driving force is required to trigger the formation of hcp martensite, which means the chemical composition of the alloy at $M_s$ temperatures must be located sufficiently below $T_0$. The diffusionless formation of hcp martensite may still be mechanically induced for alloys at temperatures above $T_0$ if enough stress is applied to increase the relative difference in the Gibbs free energy, thus shifting the $T_0$ up. If the Mn content for the shifted $T_0$ is greater than that in the alloy, a positive driving force can be obtained.
An alloy composition should be intact during the martensitic transformation. The driving force for the martensitic transition is, therefore, calculated by taking the difference between the Gibbs energies of the two phases at the alloy composition. The driving force determined this way exhibits no clear correlation with mechanical properties of interest. Twinning induced plasticity (TWIP) steels, on the other hand, are strengthened by the formation of deformation twins in the fcc matrix. If the twins are assumed to be embryos of the hcp phase, then their formation is related to the driving force for the hcp transition. Recent studies related the serrations on a stress–strain curve for TWIP steels to the Portevin–Le Chatelier effect promoted by diffusing solutes interacting with dislocations [7, 44]. The fcc alloy is not thermodynamically stable if a composition separation is expected at equilibrium. The alloy is, however, stable if no such separation is possible to further minimize the energy. The difference between the lowest energy for the fcc phase and the corresponding energy value for the hcp phase determines the globally stable driving force for the hcp transformation. In this work, the driving force was determined by taking the lowest energies of the two phases at the alloy composition, which lie on the equilibrium planes drawn through all the composition sets if available. Note that this driving force should not be confused with that for a complete precipitation, which is determined by the difference between the energy of the matrix phase and that of the equilibrium tangent as each phase partitions to a new equilibrium composition. The present driving force is the energy difference between the two phases taken at the most stable stages independent of each other, which is determined at the alloy composition. In the present study, phase separations are hypothetically assumed to estimate the lowest possible energy of each phase.

With the addition of carbon to the Fe–Mn system, there are potentially three composition sets to consider for each phase. In the Fe–Mn–C system with up to 35 wt% Mn and 1.2 wt% C, the hcp and fcc phases both separate into an Fe-rich phase and a Mn-rich phase. It must be emphasized that, for these phases, the two composition sets occurred only in the presence of carbon in the system. No phase separation was noted in the Fe–Mn binary system. Carbon tended to partition to the Mn-rich phase rather than to the Fe-rich phase across the compositions studied. The present driving force is determined as the dimensionless Gibbs energy difference (\( \frac{-dG_m}{RT} \)), which is plotted against Mn and C contents in figure 5. \( \frac{-dG_m}{RT} \) is negative for Mn-rich systems, and rapidly turns positive with increasing carbon concentration. For example, the Fe–35Mn alloy (SFE = 45 mJ m\(^{-2}\)) falls into a negative \( \frac{-dG_m}{RT} \) region, but the Fe–30Mn–0.5C alloy falls into a positive \( \frac{-dG_m}{RT} \) region, although it has the same SFE. If a sufficiently positive driving force is needed to form deformation-induced hcp martensite or twin, Mn and C contents can be adjusted accordingly at production. This result may explain previous reports [6, 17, 43] where deformation twins were either present or absent in alloys having similar SFE values. Bouaziz et al [6] compared Fe–30Mn and Fe–22Mn–0.6C alloys with similar SFE values where, after deformation, extensive mechanical twinning was observed in the Fe–22Mn–0.6C alloy, whereas no twins were found in the Fe–30Mn alloy (figure 6). The confusion with the conventional SFE concept may be attributed to the \( \frac{-dG_m}{RT} \) value, which is negative for the Fe–30Mn alloy (=0.1) and positive to a large extent for the Fe–22Mn–0.6C alloy (+0.4).

Figures 7–9 show the empirical maximum true stress, maximum true strain and yield strength [6, 19, 25, 34] as a function of \( \frac{-dG_m}{RT} \). The maximum stress and strain here correspond to sample failure in tensile tests. The Mn and C contents in collected data varied from 12 to 30 wt% and from 0 to 1.2 wt%, respectively. A positive correlation exists between these values for the given experimental data. This proportionality between mechanical and thermodynamic properties may be related to the increased thermodynamic stability of the hcp relative to fcc phase.
Figure 7. Experimental maximum true stress versus $-dG_m/(RT)$. A dotted curve shows a trend across all the compositions, while a dashed curve indicates a trend over alloys with positive $-dG_m/(RT)$.

Figure 8. Experimental maximum true strain versus $-dG_m/(RT)$. A dotted curve shows a trend across all the compositions, while a dashed curve indicates a trend over alloys with positive $-dG_m/(RT)$.

Figure 9. Experimental yield strength versus $-dG_m/(RT)$. A dotted curve shows a trend across all the compositions, while a dashed curve indicates a trend over alloys with positive $-dG_m/(RT)$.

4. Conclusions

SFE in the Fe–Mn–C system was calculated using the model developed by a CALPHAD approach. SFE is always constant ($32.7 \text{ mJ m}^{-2}$) at $T_0$, independent of composition and temperature, provided that the other parameters are intact. The experimental limits for the thermal hcp formation and the mechanical hcp formation were separated by the SFE determined at $T_0$. The driving force for transition to the hcp phase was determined as $-dG_m/(RT)$, the system value with consideration of multidimensional miscibility gaps. The proportionality of experimental maximum true stress, maximum true strain and yield strength to $-dG_m/(RT)$ implied the need for positive $-dG_m/(RT)$ to promote the formation of mechanical twins.

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