

A TREATMENT OF PARAEQUILIBRIUM THERMODYNAMICS IN AF1410 STEEL USING THE THERMOCALC SOFTWARE AND DATABASE

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ABSTRACT It is demonstrated that the ThermoCalc computer program and database can be used for calculation of phase paraequilibrium provided proper modifications of phase descriptions have been made. This procedure has been used to analyze precipitation of M_2C carbides from a "paraequilibrium" two-phase ferrite/cementite mixture in standard and series of modified AF1410 steels. It is found that from the standpoint of achieving fine dispersion of M_2C phase and thus improved strength properties, it is beneficial to make a complete substitution of chromium with molybdenum in steels of this class.

INTRODUCTION

High Co-Ni secondary hardening steels such as AF1410 are known to have an exceptionally good combination of strength and toughness. Superior properties are associated with a fine-scale precipitation of M_2C carbides ($M = Cr, Fe, Mo$). At the condition of optimum combination of strength and toughness the steel is in a slightly overaged condition, and hence its strength is inversely proportional to the average particle spacing. The average particle spacing, on the other hand, is the result of a competition between nucleation and subsequent growth of the particles. A high nucleation rate gives rise to a finer dispersion and improved strength properties. As recently discussed by Grujicic[1], nucleation kinetics can be enhanced by increasing the driving force for nucleation of the precipitating phase.

It is well established[2] that precipitation of M_2C carbides during the secondary hardening treatment is preceded by the formation of transient paraequilibrium cementite. The transient reaction gives rise to an undesired carbon depletion of the ferrite, which leads to a lower driving force for nucleation of the M_2C phase as shown in Fig.1. The extent of this depletion, which is a function of alloy additions, can be minimized by proper selection of alloy composition.

In this paper we present a thermodynamic analysis of nucleation of the M_2C phase from a two-phase paraequilibrium mixture of ferrite and cementite in standard AF1410 steel (14%Co, 10%Ni, 2%Cr, 1%Mo, 0.16%C, (wt.%) and in a series of modified AF1410 alloys with the same amount of Co, Ni, and C and various Cr and Mo additions. The amount of Cr and Mo is balanced to give a fixed sum of mole fractions of these two elements. All the calculations have been performed using the ThermoCalc computer program and database[3]. The analysis involves an assessment of paraequilibrium between ferrite and cementite, which is not feasible with the current version of

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ThermoCalc. Here we introduce a treatment of the paraequilibrium condition, which can be carried out using a modified version of ThermoCalc.

CALCULATION PROCEDURE

The ThermoCalc database is based on a thermodynamic model originally developed by Sundman and Ågren[4]. The model treats, in a unified manner, phases with various number of sublattices. Composition variables are presented as lattice site fractions, which describe element partitioning between sublattices and the fractional occupancy of each sublattice. The sum of site fractions in each sublattice is by definition equal to unity. The model gives separate accounts of various contributions to the excess Gibbs free energy of a phase such as exchange energy and energies associated with atomic and magnetic ordering. The molar Gibbs free energy of phase Φ with two sublattices occupied respectively with elements I,J,K,... and i,j,k,... is defined as:

$$G_m^\Phi = \sum_I y_I^\Phi \sum_i y_i^\Phi G_{Ii}^{0\Phi} + RT \left[\sum_{n=1}^2 a^{(n)} \sum_m y_m^\Phi \ln y_m^\Phi \right] + G_m^{\text{RKM}} + G_m^{\text{MO}} + G_m^{\text{AO}} \quad (1)$$

where y_I^Φ and y_i^Φ are respectively the site fractions of elements I and i on two sublattices in phase Φ (subsequently the superscript Φ will be dropped to simplify notation). $G_{Ii}^{0\Phi}$ is the standard free energy of formation of Φ phase with sublattices 1 and 2 respectively occupied with elements I and i, $a^{(n)}$ is the number of sites on sublattice n ($m=1$ when $n=1$ and $m=i$ when $n=2$). G_m^{RKM} is the exchange excess free energy, which is expressed using a Redlich - Kister - Muggianu type (RKM) series expansion[5]. G_m^{MO} and G_m^{AO} are respectively the excess free energies due to magnetic and atomic ordering. The excess free energy G_m^{RKM} can be defined as:

$$G_m^{\text{RKM}} = \sum_I y_I \sum_{\substack{j \\ j \neq I}} y_j y_j \left[L_{Ij}^0 + (y_i - y_j) L_{Ij}^1 + \dots \right] + \sum_i y_i \sum_{\substack{j \\ j \neq i}} y_j y_j \left[L_{ij}^0 + (y_I - y_j) L_{ij}^1 + \dots \right] \\ + \sum_i y_i \sum_{\substack{j,k \\ j,k \neq i}} y_j y_k y_k \left[L_{i,j,k}^0 \right] + \sum_I y_I \sum_{\substack{j,k \\ j,k \neq I}} y_j y_k y_k \left[L_{I,j,k}^0 \right] \quad (2)$$

where $L_{Ii,j}^0$ and $L_{Ii,j}^1$ are respectively regular and subregular i-j two-element interaction parameters in the presence of element I on the other sublattice. Likewise, $L_{I,j,i}^0$ and $L_{I,j,i}^1$ are respectively regular and subregular I-J two-element interaction parameters with element i residing on the other sublattice; $L_{I,J,K,i}^0$ and $L_{I,i,j,k}^0$ are respectively the I-J-K and i-j-k three element interaction parameters in the presence of i and I respectively on the other sublattice.

The magnetic contribution to the excess free energy G_m^{MO} has the form originally suggested by Inden[6] and further developed by Hillert and Jarl[7]:

$$G_m^{\text{MO}} = R T \ln(\beta + 1) f(\tau) \quad (3)$$

where β is the Bohr magneton; $\tau = T/T_C$; T is the temperature and T_C the Curie temperature; $f(\tau)$ has been defined as follows:

$$\text{For } \tau < 1 \quad f(\tau) = -0.90530 \tau^{-1} + 1.0 - 0.153 \tau^3 - 6.8 \cdot 10^{-3} \tau^9 - 1.53 \cdot 10^{-3} \tau^{15}$$

$$\text{For } \tau > 1 \quad f(\tau) = -6.417 \cdot 10^{-2} \tau^6 - 2.037 \cdot 10^{-3} \tau^{15} - 4.278 \cdot 10^{-4} \tau^{25}$$

β and T_C have the following compositional dependence:

$$\beta = \sum_i y_i \sum_j y_j \beta_{ij} + \sum_i y_i \sum_{j \neq i} \sum_k y_j y_k [\beta_{ikj}^0 + (y_i - y_j) \beta_{ikj}^1 + \dots] \\ + \sum_i y_i \sum_{j \neq i} \sum_k y_i y_j [\beta_{ijj}^0 + (y_i - y_j) \beta_{ijj}^1 + \dots] \quad (4)$$

and

$$T_c = \sum_i y_i \sum_j y_j T_{ij}^c + \sum_i y_i \sum_{j \neq i} \sum_k y_j y_k [T_{ikj}^{0c} + (y_i - y_j) T_{ikj}^{1c} + \dots] \\ + \sum_i y_i \sum_{j \neq i} \sum_k y_i y_j [T_{ijj}^{0c} + (y_i - y_j) T_{ijj}^{1c}] \quad (5)$$

where:

$$\beta_{ij}, \beta_{ikj}, \beta_{ijj} \text{ and } T_{ij}^c, T_{ikj}^c, T_{ijj}^c$$

are magnetic parameters analogous to ${}^0G\Phi_{ij}$, L_{ij} and L_{ijj} in equations (1) and (2) respectively. The effect of atomic ordering can in principle be similarly treated, but since the ThermoCalc database on our disposal did not contain information pertaining to atomic ordering, we will exclude the term G_m^{AO} from further consideration.

The current version of ThermoCalc program is capable of dealing only with cases of unconstrained equilibrium, where all elements in the system are permitted to partition to an extent which corresponds to a minimum in the total free energy. In this case, the chemical potential of an element is constant throughout the system. It is not possible, however, to treat any kind of constrained equilibrium, where some elements do not partition, although, we understand that paraequilibrium will be treatable in a pending version of ThermoCalc. Here, we present a treatment of paraequilibrium, which can be performed using the current version of the ThermoCalc program. The treatment involves the introduction of fictitious elements and "paraequilibrium" phases, which are defined using corresponding legitimate elements and phases which are recognized by the ThermoCalc database. After substituting equation (1) into equation (2) and rearranging, one obtains:

$$G_m^\Phi = y_i \left[\sum_j y_j G_{ij}^0 + \sum_{j \neq i} \sum_k y_j y_k [L_{ijj}^0 + (y_i - y_j) L_{ijj}^1 + \dots] + \sum_{j \neq i} \sum_{k \neq j} \sum_l y_j y_k y_l [L_{ijk}^0 + a^{(1)} RT \sum_j |ny_j|] \right] \\ + y_j \left[\sum_l y_l G_{lj}^0 + \sum_{l \neq j} \sum_k y_l y_k [L_{ljj}^0 + (y_j - y_l) L_{ljj}^1 + \dots] + \sum_{l \neq j} \sum_{k \neq l} \sum_m y_l y_k y_m [L_{ljk}^0 + a^{(1)} RT \sum_j |ny_l|] \right] \\ + \sum_{j \neq i} y_i y_j \left[\sum_l y_l L_{ikj}^0 + (y_i - y_j) \sum_l y_l L_{ikj}^1 + \dots \right] + a^{(2)} RT \sum_j y_j |ny_j| + G_m^{MO} \quad (6)$$

When elements l on sublattice 1 do not partition, y_l are fixed and it is therefore convenient to introduce a fictitious element $M = \sum_j y_j l$. Then the phase Φ has the constitution $M_{i,j}$ and accordingly equation (6) can be written as:

$$G_m^\Phi = \sum_i y_i G_{M:i}^0 + a^{(2)} RT \sum_i y_i |ny_i| + \sum_{i \neq j} y_i y_j [L_{M:ij}^0 + (y_i - y_j) L_{M:ij}^1 + \dots] + G_m^{MO} \quad (7)$$

where $G_{M:i}^0$, $L_{M:ij}^0$ and $L_{M:ij}^1$ are respectively the modified lattice stability and exchange interaction parameters. Likewise equations (4) and (5) can be rearranged to give:

$$\beta = \sum_i y_i \left[\sum_j y_j \beta_{ki} + \sum_{l \neq j} y_l y_j \beta_{l,j,i}^0 + (y_i - y_j) \beta_{l,j,i}^1 + \dots \right] + \sum_{l \neq j} y_l y_j \left[\sum_i y_i \beta_{ki,l}^0 + (y_i - y_j) \sum_i y_i \beta_{ki,l}^1 \right]$$

$$= \sum_i y_i \beta_{M,i} + \sum_{l \neq j} y_l y_j \left[\beta_{M:l,i}^0 + (y_i - y_j) \beta_{M:l,i}^1 + \dots \right] \quad (8)$$

and

$$T_C = \sum_i y_i \sum_j y_j T_{ij}^C + \sum_{l \neq j} y_l y_j \left[T_{l,j,i}^{0C} + (y_i - y_j) T_{l,j,i}^{1C} + \dots \right] + \sum_{l \neq j} y_l y_j \left[\sum_i y_i T_{li}^{0C} + (y_i - y_j) \sum_i y_i T_{li}^{1C} \right]$$

$$= \sum_i y_i T_{M,i}^C + \sum_{l \neq j} y_l y_j \left[T_{M:l,i}^{0C} + (y_i - y_j) T_{M:l,i}^{1C} + \dots \right] \quad (9)$$

Substitution of equations (8) and (9) in equation (3) and then in equation (7) gives the molar Gibbs free energy of phase Φ , expressed in terms of lattice stability and excess quantities of a fictitious element M fully occupying sublattice 1. If this phase is in equilibrium with another phase, which also has sublattice 1 occupied solely with element M, one can talk about a paraequilibrium condition. In this case the condition of equal chemical potential in the system is valid only for the partitioning elements i, j, \dots and for element M, but not for non-partitioning elements l, j, \dots .

To summarize, a treatment of paraequilibrium entails the introduction of a fictitious element $M = \sum y_l$ and a modified description of phases in terms of M-based lattice stabilities and excess quantities. The latter are readily defined in terms of corresponding quantities for non-partitioning elements l, j, k, \dots included in the ThermoCalc database.

RESULTS AND DISCUSSION

In this section we analyze the effect of precipitation of paraequilibrium cementite at 510°C on the driving force for nucleation of the M_2C phase in standard and modified AF1410 alloys. For standard AF1410 steel, Fig.1 shows (solid points) that the carbon content in ferrite decreases from 0.16 to 0.0021 as a result of paraequilibrium cementite precipitation. Consequently the driving force

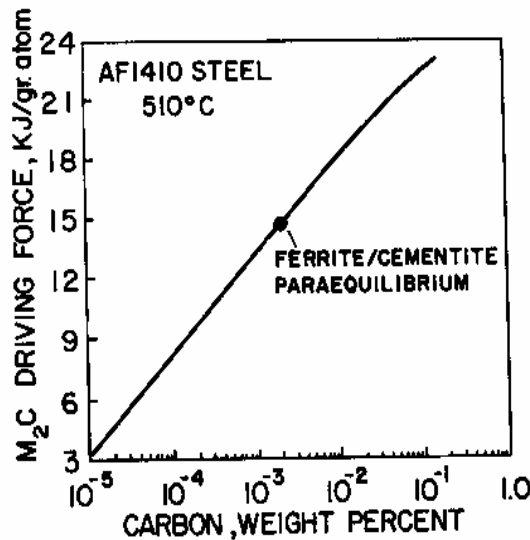


FIG. 1
Effect of carbon on the driving force for nucleation of M_2C phase in AF1410 steel at 510°C.

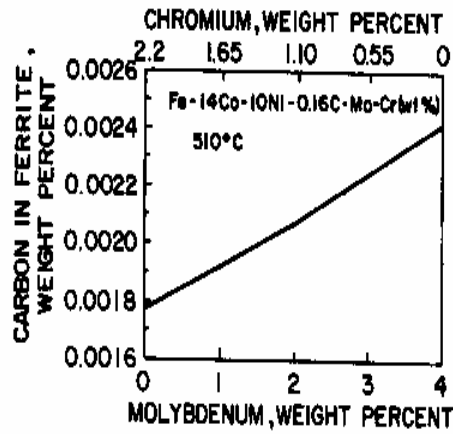


FIG.2.

Effect of combined additions of chromium and molybdenum on the carbon content in ferrite in a series of Fe-14Co-10Ni-0.16C-Mo-Cr (wt%) alloys at 510°C. The ferrite is considered to be in paraequilibrium with cementite.

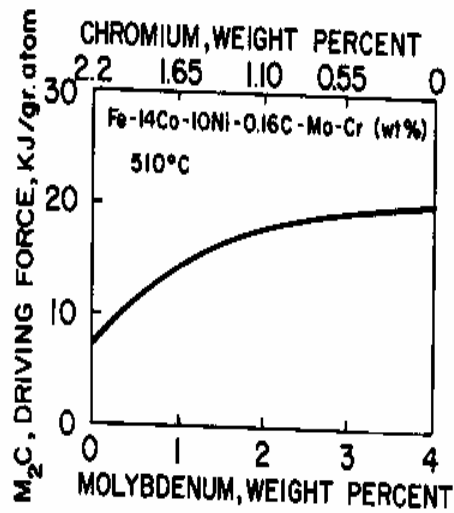


FIG.3

Effect of combined additions of chromium and molybdenum on the driving force for nucleation of M₂C phase in a series of Fe-14Co-10Ni-0.16C-Mo-Cr (wt%) at 510°C. The ferrite is considered to be in paraequilibrium with cementite.

for nucleation of M_2C is reduced by as much as 35%. Figures 2 and 3 show respectively the effect of substitution of Cr for Mo on the carbon content of ferrite (in paraequilibrium with cementite) and on the driving force for nucleation of the M_2C phase under the condition of fixed combined mole fraction $X_{Cr}+X_{Mo}=0.024$. Both the carbon content in ferrite and the driving force for nucleation of M_2C are maximum on the molybdenum side, suggesting that in order to maximize strength in these alloys via refinement of particle spacings, a complete substitution of Cr with Mo should be preferred. It should be noted however, that the increase in the driving force for M_2C nucleation with Mo, is mainly a result of the higher stability of Mo_2C relative to Cr_2C and only partly due to the fact that the effect of carbon depletion in ferrite due to precipitation of paraequilibrium cementite is more pronounced in the presence of Cr than Mo. This can be seen by comparing Figures 2 and 3. While the carbon content in ferrite is increased by approximately 35% from the Cr to the Mo side, the driving force for M_2C nucleation increases by 250% over the same composition range.

There are other reasons for substituting chromium for molybdenum in these alloys. The transient cementite phase is very detrimental to toughness and must be completely dissolved. In fact the standard heat treatment for the AF1410 steel, $510^\circ C/5h$, which gives rise to an optimum combination of strength and toughness, has been designed to ensure a full dissolution of this phase. This dissolution is hampered, however, by partitioning of Cr and Mo, which make cementite more stable. Fast diffusing Cr, which is also a more effective cementite stabilizer than Mo, makes cementite dissolution more difficult, entailing higher temperatures and longer times. These, in turn, give rise to a greater extent of M_2C overaging and hence lower strength properties in chromium containing alloys.

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