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# The determining role of magnetic field in iron and alloy carbide precipitation behaviors under the external field

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ABSTRACT

A combined approach to calculate the thermodynamic properties of iron and alloy carbides including the thermal and magnetic contribution is derived. Special emphasis is placed on the role of Fe and Mo to the Gibbs free energy. Lower Mo concentration in the carbides corresponds to a higher thermal Gibbs free energy change. The higher Fe content and external magnetic field greatly increase the induced magnetization, reducing the magnetic Gibbs free energy substantially and therefore increase the formation temperature. The stability of $M_2C$ and $M_3C$ are mainly determined by the thermal factors, whereas magnetic field has a predominant contribution for $M_6C$.



Iron or alloy carbides play an important role in heat resistant steels, including those which are microalloyed or secondary-hardened for service at elevated temperatures. $M_3C$, $M_2C$, $M_6C$ are the most important precipitate phases in alloyed steels. As ferromagnetic alloy carbides have different magnetization, the introduction of a magnetic field can effectively change their stability by altering their Gibbs free energy, and thus affect their precipitating behaviors. Consequently, the final material properties can be altered potentially in a controlled manner. Previous result have showed that $M_2C_5$ [1,2], $M_6C$ [3,4], $M_7C_3$ and $M_{23}C_6$ [5] were promoted to precipitate earlier under high magnetic field compared with traditional heat treatment. Magnetic-field-induced precipitation in alloys, especially for the steels used under the extreme conditions of high magnetic field and intermediate temperature, is of significant scientific and technological importance. For example, improved descriptions of the Plasma Wall Interaction in a magnetic confinement Tokamak [6] is generally considered necessary to solve the key magnetism problem in International Thermonuclear Experimental Reactor. This is the basis for the development of fusion energy, in which steels works under the extreme conditions of high magnetic field and intermediate temperature.

The question of how to explain magnetic-induced precipitation behaviors is discussed from several different standpoints. The majority of the energy analysis, which is the combination of temperature and magnetization, is focused so far on magnetic free energy calculation at $T = 0$ K only [7–9]. The magnetic free energy neither takes temperature effects into account nor considers differences among the same type of carbide. The second standpoint is the traditional thermodynamic assessment which describes the thermal Gibbs free energy ($\Delta G_V(T,X)$) as functions of temperature and composition. Thermodynamic calculations of multicomponent alloy equilibria are today a well-established method for alloy development, such as MTDATA [10], JMat-Pro [11], and Thermo-Calc [12] software. Such software is very useful for extrapolations into unknown regions and for planning of experimental work in systems that include six to ten components and two to four phases in equilibrium. However, when external field is applied to the system, the influence of magnetic field on the phase stability needs to be considered.

The precipitation of the alloy carbide $(Fe, Mo)_6C$ was effectively promoted when a magnetic field of 12 T was applied during quench-tempering [13] and the bainite transformation [3,14] of Fe-0.28C-3.0Mo (wt%). On the other hand, magnetic fields have no obvious influence on $(Fe, Mo)_2C$ or $(Fe, Mo)_3C$. This leads to an ambiguous notion that the external field has the same effect on $M_2C$ and $M_3C$ (M = Fe, Mo), ignoring the fact that the different carbides have distinct composition and structure which both result in different degree of influence by a high magnetic field. For example, there are three kinds of known structures $Fe_2Mo_4C$ [15], $Fe_3Mo_3C$ [16] and $Fe_4Mo_2C$ [17] in $M_6C$, each of the

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carbides corresponds to different Fe and Mo content and then, results in distinct thermal and magnetic Gibbs free energies. It is the main purpose of this paper to extend a detailed study of the thermodynamic assessment on the magnetic-field-induced precipitation behaviors of three types of carbide $(Fe, Mo)_2C$, $(Fe, Mo)_3C$ and $(Fe, Mo)_6C$. It is sufficient for qualitative, and in many cases even a quantitative understanding of the magnetic-field-induced stabilities and specific features in the physical properties of different carbides.

The total magnetic moments per unit cell of transition carbides have been obtained using first-principles calculations. All-electron full-potential linearized augmented plane wave method was used as embodied in the WIEN2K code [18]. The exchange-correlation potential was calculated using the generalized gradient approximation via the scheme of Perdew-Burke-Ernzerhof 96 [19]. The electronic wave functions were sampled with 72, 72, 120, 47, 72 and 72 k points in the irreducible Brillouin zone of ε-$Fe_2C$, FeMoC, $Fe_2MoC$, $Fe_2Mo_4C$, $Fe_3Mo_3C$ and $Fe_4Mo_2C$, respectively. The sphere radii (muffin tin) were 2.22, 2.10 and 1.86 a.u. for iron, molybdenum and carbon atoms, respectively. The use of the full potential ensured that the calculation was completely independent of the choice of the sphere radii. Different plane waves were tested, e.g. 2433–2453 grids for $M_6C$, 248–260 for $M_2C$ (ε-$Fe_2C$ and FeMoC) and 1668–1720 for $M_3C$ ($Fe_3C$, $Fe_2MoC$ and $FeMo_2C$), respectively. In this work, the Fe, Mo1 and Mo2 Wyckoff sites in $Fe_2Mo_4C$ were correspondingly replaced with Mo, Fe2 and Fe1 sites to obtain the structure of $Fe_4Mo_2C$. The crystal structures for alloy carbides $Fe_2Mo_4C$ and $Fe_4Mo_2C$ are displayed in reference [20]. The Wyckoff positions 16d/32e are occupied by Mo or Fe atoms for $Fe_2Mo_4C$ and $Fe_4Mo_2C$.

Using the thermodynamic software named MTDATA from the UK's National Physical Laboratory, the equilibrium phases for each steel could be calculated [10]. For all the phases, precipitate occurs by diffusion of both substitutional and interstitial atoms, and it is expected, therefore, that the Gibbs free energy of the system is minimized. The program MTDATA was used to calculate each phase using this criterion. The $\Delta G_V(T,X)$ of $M_2C$, $M_3C$ and $M_6C$ at constant pressure were calculated with TCAB database for steels version 1.0. It has been found that $M_2C$, $M_3C$ and $M_6C$ carbides formed not only at the interphases boundaries but within the bainitic ferrite plates [14] or laths regardless of whether high magnetic field was applied or not. In the simplest cases, the parent phase is identified as the ferrite and the product phases as $M_2C$, $M_3C$ or $M_6C$. The step of temperature during the calculation was 10 K. In order to comprehensively estimate three types of carbide, we calculated ten carbides $M_2C$ ($Mo_2C$, FeMoC, ε-$Fe_2C$ and η-$Fe_2C$), $M_3C$ ($Fe_3C$, $Fe_2MoC$ and $FeMo_2C$) and $M_6C$ ($Fe_2Mo_4C$, $Fe_3Mo_3C$, $Fe_4Mo_2C$). First taking the equilibrium phase for each type of carbide as reference we obtain the thermal Gibbs free energies of other carbides by means of changing the molecular weight. We note that there are several discontinuity in the phase transformation which should be taken into account during equilibrium calculation. However, such discontinuities in the curve are not considered here since the effect in the final determining factor is quite small.

When magnetic field is applied, the resulting total Gibbs free energy change $\Delta G_{total}(T,X,B)$ should be classified into two terms in Eq. (1): $\Delta G_V(T,X)$ which is determined by the temperature and composition, and the magnetic Gibbs free energy$\Delta G_M(T,B)$, where $T$, $X$ and $B$ correspondingly is the temperature, composition and external field strength.

$$\Delta G_{total}(T,X,B) = \Delta G_V(T,X) + \Delta G_M(T,B) \quad (1)$$

The theoretical temperature dependence of $\Delta G_V(T,X)$ is shown in Fig. 1 for three types of carbides. The equilibrium compositions of $M_2C$, $M_3C$ and $M_6C$ predicted using MTDATA are $Mo_{0.67}C_{0.33}$, $Fe_{0.75}C_{0.25}$ and $Fe_{0.41}Mo_{0.44}C_{0.14}$, which are close to $Mo_2C$, $Fe_3C$ and $Fe_3Mo_3C$, respectively. For $M_2C$, previous experimental results showed that three carbides ($Mo_2C$, ε-$Fe_2C$ and η-$Fe_2C$) are commonly observed in steel. In order to comprehensively describe $M_2C$, the carbide FeMoC is included in the theoretical calculation. The substitution of Mo by Fe shows a clear difference in $\Delta G_V(T,X)$ for $Mo_2C$, FeMoC, ε-$Fe_2C$ and η-$Fe_2C$ in Fig. 1 (dotted lines). It is noteworthy that $\Delta G_V(T,X)$ is equal for ε-$Fe_2C$ and η-$Fe_2C$ (both marked with $Fe_2C$) because they have the same molecular weight. Comparing the energy results for $M_3C$ with the Mo substituting Fe at constant pressure (Fig. 1, dashed lines), it was found that the predicted theoretical curves of $Fe_2MoC$ and $FeMo_2C$ fall below the line of $Fe_3C$. The thermal Gibbs free energies in the other carbides $Fe_2Mo_4C$, $Fe_3Mo_3C$ and $Fe_4Mo_2C$ have been obtained (Fig. 1, solid lines). The reduction of the thermal free energy follows the sequence: $Fe_2Mo_4C > Fe_3Mo_3C > Fe_4Mo_2C$. Overall it is reasonable to find that higher Mo concentration carbides are energetically favorable for the three types of $M_2C$, $M_3C$ and $M_6C$. It is also in good agreement with the previously reported result that the stability can be improved by an addition of Mo atom occupying the 8c site [21].

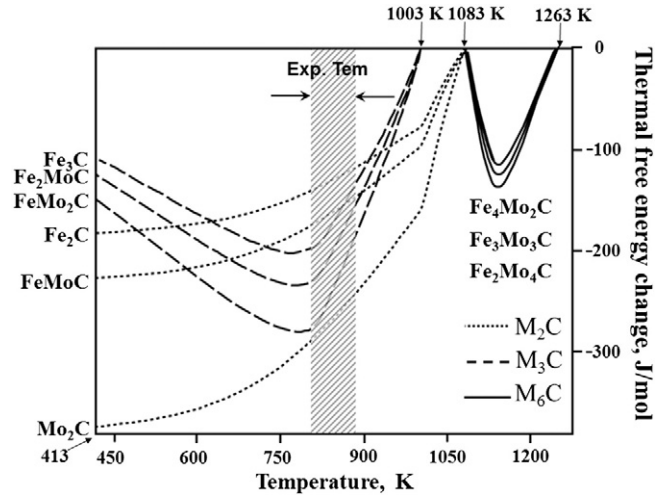


**Fig. 1.** Comparison of the calculated changes in chemical free energy of $M_2C$ ($Fe_2C$, FeMoC, $Mo_2C$), $M_3C$ ($Fe_3C$, $Fe_2MoC$, $FeMo_2C$) and $M_6C$ ($Fe_2Mo_4C$, $Fe_3Mo_3C$, $Fe_4Mo_2C$) in Mo-containing steel during elevated temperature tempering at constant pressure. Thermodynamic assessment performed using MTDATA. The shaded area represents the experimental range of 803 to 883 K.

Furthermore, as shown in Fig. 1, $M_6C$ ($Fe_2Mo_4C$, $Fe_3Mo_3C$ and $Fe_4Mo_2C$) first precipitates upon cooling at 1263 K. At lower temperature it coexists with austenite and is expected to dissolve at 1083 K. $M_6C$ appears beyond the scope of the previous experimental temperature range of 803 [13,14] – 883 K [3]. In other words, when the magnetic field was not applied, only $M_2C$ and $M_3C$ were precipitated which is consistent with the previous experimental results (shadow area in Fig. 1) [3,22].

The semi-empirical models currently used in the CALPHAD method consider the magnetic contribution to the Gibbs energy using the Inden-Hillert-Jarl model [23,24], it uses analytical expressions obtained from numerical fits to known equilibrium data. Another method which is supplementing experimental data sets with the results of the first-principles calculations has been well developed. For iron carbides, the calculated thermodynamic properties (0 K) of iron carbides have been extensively evaluated according to the formation energy [8,25] or formation enthalpy [26]. However, it should be noted that magnetism, which is often ignored, can be a determining influence on the stability of carbides [27]. The first-principles magnetic free energy is calculated for ferromagnetic α-Fe employing either the spin quantum Monte Carlo (QMC) [25] or the improved random phase approximation approach [28] and for $Fe_3C$ using QMC approach [25]. CALPHAD or another hybrid method combining first-principles calculations are excellently suited to describe the temperature dependences of free energy. However, they are not currently capable of taking into account of an applied magnetic field.