Magnetic field and stability of alloy carbides

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Phase Transformations and Complex Properties Group

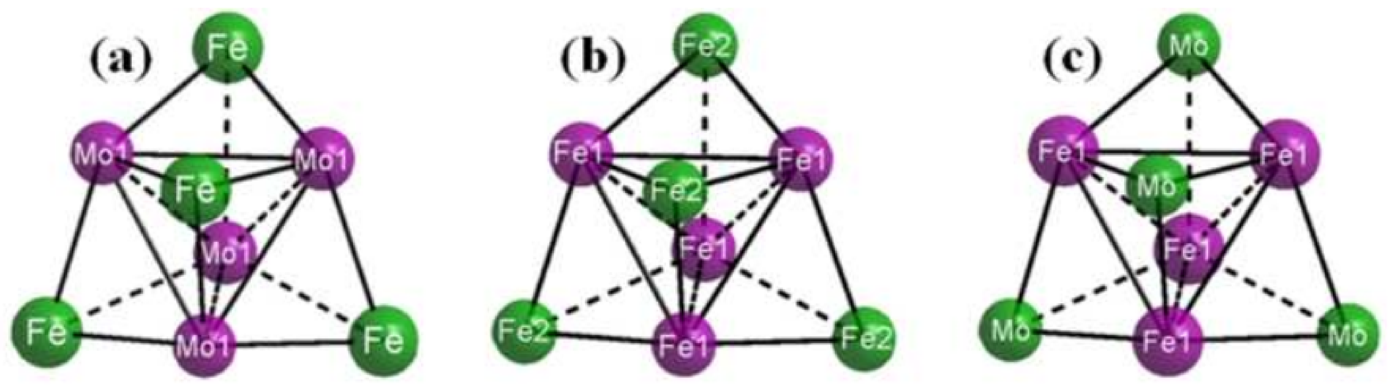
Summary

First-principle calculations and Weiss molecular field theory have been combined with thermodynamic data, allowing us to calculate the thermodynamic properties of iron and alloy carbides including the magnetic contribution. Special emphasis is placed on the role of Fe and Mo to the Gibbs free energy in a magnetic field. 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 stability of the carbides, as reflected by the higher 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.

The paramagnetic Mo atom disturbed the order of magnetic moment and resulted in a decrease in the Curie temperature for alloy carbide $Fe_{6-x}Mo_xC$. The temperature dependence of the magnetic moment and saturation magnetization of different Wyckoff positions of Fe atom, as well as the saturation or induced magnetization of $Fe_{6-x}Mo_xC$, decreases with increasing temperature. The higher Fe content and external magnetic field could greatly increase the magnetization of alloy carbides. Two kinds of stella quadrangula lattices are employed to account for the total magnetism which is derived from the contribution of different Wyckoff sites of Fe atoms and Fe-C distances. The magnetic free energy contribution increases with increasing magnetic field strength. The calculated total free energy taking into account the magnetic field, temperature and composition is sufficient to provide quantitative agreement with experiment. The investigation of magnetic-field-induced precipitation behaviours could contribute to a better understanding the phase transformation mechanism underlying magnetic field in heat resistant steels.

First-principle calculation of different alloy carbides

The total magnetic moments per unit cell of transition carbide have been obtained using first principle calculation [1, 2]. All-electron Full-potential Linearized Augmented Plane Wave (FPLAPW) method was used as embodied in the WIEN2K code [3]. The exchange-correlation potential was calculated using the generalized gradient approximation (GGA) via the scheme of Perdew *et al.* [4]. The electronic wave functions were sampled with 47 k, 72 k and 72 k points in the irreducible Brillouin zone of Fe_2Mo_4C, Fe_3Mo_3C and Fe_4Mo_2C,respectively. The sphere radii (muffin tin) R_{MT} = 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 $Fe_{6-x}Mo_xC$. Fe_4Mo_2C is less commonly observed in steel and, there is no reference for the details of structure data. In this work, the Fe, Mo1 and Mo2 Wyckoff sites in Fe_2Mo_4C is correspondingly replaced with Mo, Fe2 and Fe1 sites to obtain the structure of Fe_4 Mo_2C, respectively.



Stella Quadrangula (SQ) lattice of Fe_3Mo_3C and the pseudo-SQ lattices for Fe_2Mo_4C and Fe_4Mo_2C carbides.

Weiss molecular field theory

The calculated magnetic moments from the first-principle calculation at 0 K, 0 Pa are combined with Weiss molecular field theory [5]. The magnetisation a function of temperature can be expressed as;

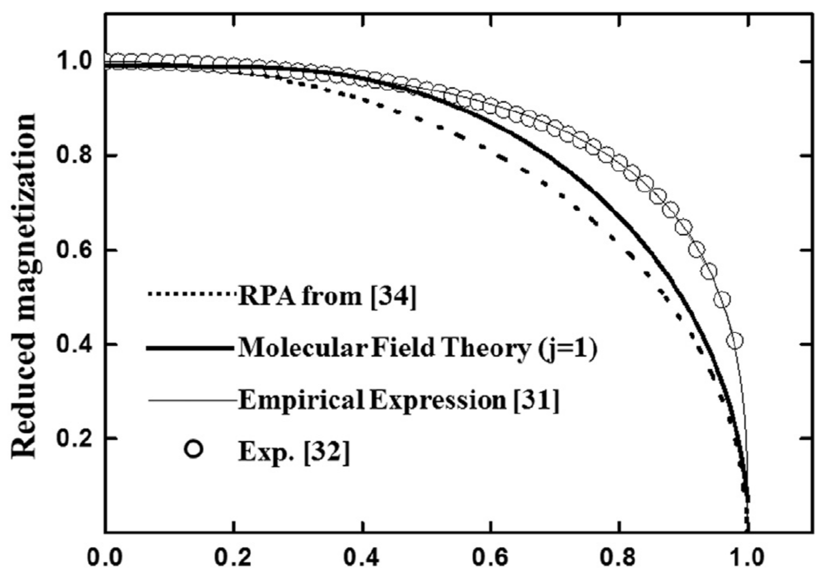
$$M_i = NmB_j\left[\frac{m(B+\lambda M_{i-1}}{kT_i}\right] \quad (1)$$

where M_i is the magnetisation at the temperature T_i, $B_j\left[\frac{m(B+\lambda M_{i-1}}{kT_i}\right]$ the Brillouin function, k the Boltzman constant and λ is the molecular field constant.

The temperature dependence of the magnetisation saturation of iron was determined using;

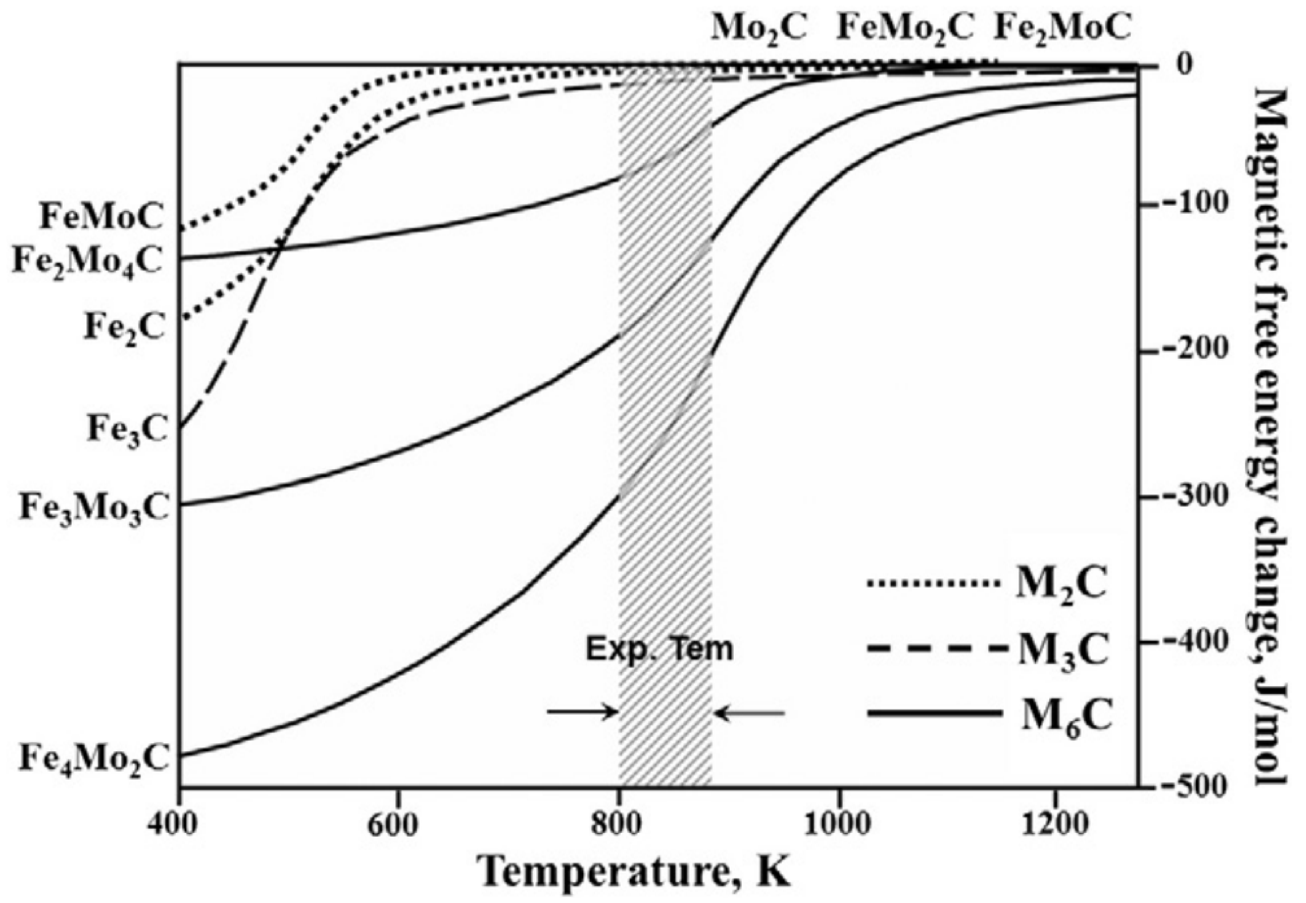
$$M_i(T) = [1 - s(T/T_C)^{\frac{3}{2}} - (1-s)(T/T_C)^4]^{\frac{1}{3}} \quad (2)$$

where s is 0.35 and the Curie temperature T_C=1044 K.



Comparison of approximations for the reduced magnetization (M/M_0) and experimental data.

Calculation Results



Free energy contribution due to magnetism in a 12 T magnetic field.

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Carbide types	Magnetic field B = 0 T	B = 12 T	Change ΔT K
η-Fe_2C	1082.5	1085.5	3
Fe_3C	1003.5	1011	7.5
Fe_2Mo_4C	1263	1266	3
Fe_3Mo_3C	1263	1274	11
Fe_4Mo_2C	1263	1276	13

Conclusions

The influence of high magnetic field on alloy carbide $Fe_{6-x}Mo_xC$ was investigated by means of a hybrid method combining thermodynamic data from MTDATA, first-principle calculation and Weiss molecular field theory. The magnetic-field-induced effect was analysed by coupling the temperature, external magnetic field and composition. The relationship and possible correlations between magnetism and microstructure have been investigated.

- External magnetic field and the higher Fe atom content in alloy carbides $Fe_{6-x}Mo_xC$ results in an increase in the Curie temperature. The degree to which the alloy carbides are influenced by the external field is in the sequence of $Fe_4Mo_2C > Fe_3Mo_3C > Fe_2Mo_4C$.
- The total magnetic moment is determined by the combined effect of the two kinds of SQ lattices, with different Wyckoff sites of Fe atoms and Fe-C distances.
- The magnetic moment and saturation magnetization of different Wyckoff positions of Fe atom in $Fe_{6-x}Mo_xC$ decreased with increasing temperature. The higher Fe content and external magnetic field could greatly increase the induced magnetization and thus, reduce the magnetic Gibbs free energy substantially.
- The thermal and magnetic field both influence the stability of alloy carbides, but magnetic field has a predominant effect during the whole experimental temperature range for M_6C.

This work quantitatively analyses the relative stability of iron and alloy carbides. By considering the thermal and magnetic Gibbs free energy we can provide a more accurate description for the influence of magnetic field on precipitation behaviour of carbides. Temperature and composition are the main determinates of the stability of M_2C and M_3C carbides across the whole temperature range, whereas the magnetic effect can have a dominant contribution to Fe_2Mo_4C, Fe_3Mo_3C and Fe_4Mo_2C when the temperature is lower than 1083 K with a 12 T field.

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