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Stability of binary and ternary $M_{23}C_6$ carbides from first principles

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ABSTRACT

First-principles calculations were performed to study the phase stability of $M_{23}C_6$, (M = V, Cr, Mn, Fe, Co, Ni) and the solubility of *d*-impurities (Fe, Co, Ni, W) in $Cr_{23}C_6$, which is the most prevalent carbide in chromium steels. Our results correctly predict the relative stability of binary carbides, among which the most stable compounds are $V_{23}C_6$, $Cr_{23}C_6$ and $Mn_{23}C_6$. Stability of the $M_{23}C_6$ and MC carbides was related to the M*d*-filling, where the M–M and M–C bonds provide the cohesive properties, respectively. We demonstrated that iron and nickel should always be present in $Cr_{23}C_6$, where their concentrations may reach 50 at.% and 30 at.%, respectively. To predict the ways to control the carbide stabilization and distribution in iron matrix, both of which govern the microstructure and mechanical properties of high-alloy steels, we also investigated the effect of tungsten addition on the stability of quaternary carbides, namely $(Cr, W, M)_{23}C_6$ (M = Fe, Co, Ni). We found that tungsten strongly enhances the solubility of iron and nickel in chromium carbide, but it does not affect the cobalt solubility. A similar stabilizing effect was predicted for molybdenum, and it can be suggested that both tungsten and molybdenum should accelerate the formation of $M_{23}C_6$ and influence the kinetics of carbide precipitation.

1. Introduction

Transition metal carbides with different M/C ratio, such as MC, M_3C, M_3C_2, M_5C_2, M_6C, M_7C_3 and $M_{23}C_6$ can be present in steels affecting appreciably their microstructure and mechanical properties. The strengthening effect arises due to homogenous carbide distribution in the matrix and at the grain boundaries, which enhances both dislocation hardening and sub-boundary hardening that improves creep resistance. A competition between the M_xC_y carbides with different M/C ratio and the resulting phase transformations occurs with variation in temperature and/or impurity concentration. The $M_{23}C_6$ carbides with the highest M/C ratio are formed during heat treatment by transformation of carbides with a lower M/C ratio ($M_3C \rightarrow M_2C \rightarrow M_{23}C_6$, $M_3C \rightarrow M_7C_3 \rightarrow M_{23}C_6$ or $M_3C \rightarrow M_6C$, $M_{23}C_6$) or from a solid solution [1–5]. The transition from M_3C to $M_{23}C_6$ leads to additional enhancement of wear resistance due to an increase in the carbide microhardness from 8–9 GPa to 16–18 GPa [1]. The $M_{23}C_6$ carbides were observed in carbon steels with Cr, Mn, W, Mo and V additions. In chromium steels, the main element in $M_{23}C_6$ is chromium, but other *d*-additions can substitute into the metal sublattice forming the multicomponent $(M, M')_{23}C_6$ carbides.

The $M_{23}C_6$ carbides strongly affect the stabilization of martensite substructure and, being distributed at grain boundaries, they prevent the boundary movement [6–8]. The creep resistance of steel strongly depends on the carbide composition, stability and distribution. Non-homogenous $M_{23}C_6$ precipitation has a negative effect on the creep properties and therefore it is important to prevent the coarsening of $M_{23}C_6$ precipitates for improving creep strength. The addition of tungsten slows the coarsening rate and enhances the precipitation hardening due to the presence of $M_{23}C_6$ carbides [9–14]. The solubility of iron in $Cr_{23}C_6$ sharply increases with tungsten addition, and the ternary carbide $(Fe, W)_{23}C_6$ was found in steels as concurrent with Fe_3W_3C. The Cr–Fe–W–C diagram by Goldschmidt [15] includes the $Fe_{21}W_2C_6$ phase, which corresponds to the $M_{23}C_6$ structure, where all Cr atoms are replaced by Fe and W. The formation of ternary $Fe_{21}W_2C_6$, $Cr_{21}W_2C_6$, as well as quaternary $Cr_{21}(Mo, W)_2C_6$ carbides was observed in alloys containing Cr, W and Mo.

Accurate description of the stability and solubility of *d*-elements in these carbides is crucial for understanding of the microstructure and properties of alloys with the carbide precipitates because the precipitate stability correlates with increased creep resistance [7]. The density functional theory (DFT) methods are useful to study the structural and electronic properties, as well as to predict the phase stability and impurity localization in very good agreement with experiment. The binary $M_{23}C_6$ carbides

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(M = Mn, Cr, Fe) were studied by the *ab initio* method [16–19], and $Cr_{23}C_6$ and $Mn_{23}C_6$ were found to be stable with a large negative formation energy E_{form}. For $Fe_{23}C_6$, the calculations showed a small positive E_{form}, which is even lower than those for other iron carbides – Fe_3C, $Fe_{12}C$ and Fe_6C [16]. The first-principles calculations [17] also predicted $Fe_{23}C_6$ to be more stable than Fe_3C; it was also demonstrated that the GGA approximation for exchange–correlation potential provides the results for $Fe_{23}C_6$ that are in better agreement with experiment than those obtained within GGA + U method including the on-site Coulomb interaction on Fe atom. The stability and mechanical properties of the ternary carbides $(Cr, Fe)_{23}C_6$ were investigated as dependent on the Fe concentration [17–21]. The atomistic approach based on the interatomic potentials was used to study the structural and thermodynamic properties of $(Cr, M)_{23}C_6$ and $(Fe, M)_{23}C_6$ (M = Mo, W) [21]. Both tungsten and molybdenum impurities were predicted to increase the stability of $Cr_{23}C_6$ and $Fe_{23}C_6$ and to favor hardenability.

In this paper we study the stability of binary $M_{23}C_6$ (M = V, Cr, Mn, Fe, Co, Ni), ternary $(M, W)_{23}C_6$ (M = Cr, Fe, Co, Ni) and quaternary $(M, Cr, W)_{23}C_6$ (M = Fe, Co, Ni) carbides. We discuss the effect of tungsten on the stability of $(M, Cr)_{23}C_6$ and solubility of 3*d*- transition elements.

2. Computational method

We used the projector augmented waves (PAW) method as implemented in the Vienna *ab initio* simulation package (VASP) [22,23] and the generalized gradient approximation (GGA) for the exchange correlation functional [24]. The plane waves with the kinetic energy up to 400 eV were employed to expand the electronic wave functions. The Brillouin-zone integrations were carried out on $8 \times 8 \times 8$, $10 \times 10 \times 10$ and $16 \times 16 \times 16$ k-point grids according to the Monkhorst–Pack scheme for the binary and ternary carbides, and elemental phases, respectively. We used the Methfessel–Paxton smearing with parameter $\sigma = 0.2$ eV that provides accurate description of the total energy for metals [25]. All calculations were spin-polarized that allowed us to study magnetism in these carbides. The equilibrium structures were obtained by the conjugate gradient method when the Hellmann–Feynman forces on atoms were less than 0.1 eV/Å. To study the phase stability, the formation energy was calculated as a total energy difference between carbide and constituted elements in their stable states. We have not considered the vibration contribution because of the complexity of crystal structure (there are 116 atoms in the unit cell of $M_{23}C_6$) and used the formation energy estimated at $T = 0$ K for prediction of carbide stability.

3. Results and discussion

3.1. Binary $M_{23}C_6$ carbides

The lattice parameters and atomic coordinates for binary carbides $M_{23}C_6$ (M = V, Cr, Mn, Fe, Co, Ni) are shown in Table 1 along with the previous theoretical results. The $M_{23}C_6$ carbide crystallizes in space group Fm_3m ($Z = 4$) and contains four nonequivalent metal M1 (4*a*), M2 (8*c*), M3 (32*f*) and M4 (48*h*) positions with coordinates (0,0,0), (0.25,0.25,0.25), (*x*,*x*,*x*) and (0,*y*,*y*), respectively, and carbon atoms are in (24*e*) site with coordinate (*z*,0,0). We found that the lattice parameter of $M_{23}C_6$ follows the ion radii of *d*-metal decreasing from V to Ni and increasing from Cr to Mo and W (Table 1).

In ferromagnetic $Fe_{23}C_6$ and $Co_{23}C_6$, the local magnetic moment on metal atoms strongly depends on their site location and equals 2.51 (1.63), 2.80 (2.01), 1.76 (0.74) and 2.14 (1.28) μ_B for Fe (Co) in the M1, M2, M3 and M4 sites, respectively. The largest moments correspond to the M2 site with (4M3 + 12M4) nearest neighbors followed by the M1 site with 12 M4 nearest neighbors. The metal substitutions into M3 and M4 sites, which have both the metal and carbon neighbors, demonstrate smaller magnetic moments. As a result, the average magnetic moments on the Fe (2.0 μ_B) and Co (1.2 μ_B) atoms in $M_{23}C_6$ are less than those in the corresponding metal phases (2.2 μ_B and 1.6 μ_B in bcc Fe and hcp Co, respectively) due to the carbon effect. For $Mn_{23}C_6$ we obtained two ferrimagnetic configurations that have various magnetic ordering of the Mn atoms and differ by only 4 meV/atom. The local magnetic moments on the Mn atoms in the M1, M2, M3 and M4 positions are −1.64, −2.47, 1.43 and 0.73 μ_B, respectively, for stable state with lattice parameter of 10.396 Å; and 1.46, −2.33, 1.32 and 0.59 μ_B, respectively, for a less stable state with lattice parameter of 10.381 Å. Magnetic moments of M2, M3 and M4 atoms are similar for both states, where the manganese magnetic moment of M2 is antiparallel to those of M3 and M4. Both parallel and antiparallel magnetic moments are possible for Mn in the M1 site that points out the magnetic instability known in several manganese alloys and compounds (see for example, [26,27]). Small difference in energies for these competing configurations suggests that the Mn spins on M1 sites are able to fluctuate thermally. All other $M_{23}C_6$ phases including $Cr_{23}C_6$ are nonmagnetic.

The calculated lattice parameters and fractional coordinates are in good agreement with the available experimental data and previous theoretical results. For $Cr_{23}C_6$, our calculations predict the M3, M4 and C coordinates to be $x = 0.381$, $y = 0.166$, and $z = 0.276$, whereas $x = 0.385$, $y = 0.165$, and $z = 0.275$ were obtained from experiment and close values $x = 0.3809$, $y = 0.1699$, and $z = 0.2767$ were found in *ab initio* calculations [16]. The formation energies of $V_{23}C_6$, $Cr_{23}C_6$ and $Mn_{23}C_6$ are negative and these phases are the most stable among the considered $M_{23}C_6$ carbides (Table 1). Small positive energies were obtained for $Fe_{23}C_6$ so that its formation seems possible under specific conditions. It should be noted that $Fe_{23}C_6$ was predicted [16,18] to be more stable than cementite Fe_3C, which is iron carbide that provides high strength and hardness in steel. The $Co_{23}C_6$ and $Ni_{23}C_6$ carbides have the large positive formation energies and they were not observed in steels as binary $M_{23}C_6$ phases.

The trends in stability of $M_{23}C_6$ compounds seem to be similar to those for the MC carbides with NaCl-structure where the destabilizing effect also increases with the atomic number of the transition metal across the period. The early transition metals (V, Ti)

Table 1
Lattice parameter *a* (Å), atomic coordinates (*x*, *y* and *z*) and formation energy E_{form} (meV/atom) for binary $M_{23}C_6$ carbides.

	$Ti_{23}C_6$	$V_{23}C_6$	$Cr_{23}C_6$	$Mn_{23}C_6$	$Fe_{23}C_6$	$Co_{23}C_6$	$Ni_{23}C_6$
a	11.5824	10.9520	10.5265, 10.5280[a]	10.3959 10.3966[a]	10.4642, 10.4668[a]	10.3253	10.3568
M3 (32*f*), *x*	0.3850	0.3849	0.3809	0.3820	0.3838	0.3832	0.3838
M4 (48*h*), *y*	0.1632	0.1651	0.1658	0.1603	0.1606	0.1644	0.1606
C (24*e*), *z*	0.2745	0.2732	0.2759	0.2757	0.2767	0.2766	0.2767
E_{form}	−268	−292	−105 −91[a]	−254 −250[a]	+24 +19.5[a]	+93	+96

[a] Theoretical predictions from Refs. [16,17].