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Stability and structures of the CFCC-TmC phases: A first-principles study

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ABSTRACT

The η-M_6C, γ-$M_{23}C_6$, and π-$M_{11}C_2$ phases (M = Cr, Mn and Fe) have complex cubic lattices with lattice parameters of approximately 1.0 nm. They belong to the CFCC-TmC family (complex face-centered cubic transition metal carbides), display a rich variety of crystal structures, and play in important role in iron alloys and steels. Here we show that first-principles calculations predict high stability for the γ-$M_{23}C_6$ and η-M_6C phases, and instability for the π-$M_{11}C_2$ phases, taking into account various compositional and structural possibilities. The calculations also show a wide variety in magnetic properties. The Cr-containing phases were found to be non-magnetic and the Fe-phases to be ferromagnetic, while the Mn-containing phases were found to be either ferrimagnetic or non-magnetic. Details of the local atomic structures, and the formation and stability of these precipitates in alloys are discussed.

1. Introduction

Ultra-fine or nanometer-sized precipitates are of paramount importance for the design of steels with desirable mechanical and thermo-physical properties [1–4]. For example, Taneike and co-workers revealed the importance of cubic phases, including (γ-)$M_{23}C_6$ (M = Cr, Mn, Fe) in creep-strengthening of steels [4]. γ-$M_{23}C_6$ and η-M_6C widely exist in steels which contain elements such as Cr, Mn, as well as Mo, and W [1–9]. Branagan and co-workers recently reported the importance of nano-precipitates, including γ-$M_{23}C_6$ phases, for a low-temperature super-plasticity in an iron alloy derived from a metallic glass [10,11]. Akamatsu and co-workers also revealed η-M_6C (M = Cr, Fe) phases on irradiated surfaces of Fe–Cr alloys [7]. The η'-$M_{12}C$ phases, whose structures are strongly related to η-M_6C, were also often found in these steels and alloys [1,2,6–8]. Furthermore, Masumoto and Imai reported a cubic phase in aged Fe–Co–Cr–Ni based heat-resisting alloys and they proposed this phase has a complex cubic lattice of space group *Fd*3*c* with composition (π-)$M_{11}(C,N)_2$ [8].

The ultra-fine/nano-sized precipitates provide a challenge for structural and phase analysis, especially for those 3d transition metal carbides having complicated cubic lattices with similar lattice parameters (in the range of 1.0–1.1 nm) [1–4,8]. Many experimental efforts have been made to identify these Complex Face Centered Cubic Transition-metal Carbides (CFCC-TmC, in short). The experimental determination of the composition and structures is often performed by means of electron diffraction (ED), electron microscopy (EM) and X-ray diffraction (XRD). However, in the case of the CFCC-TmC phases, experiments are hampered by the small sizes of the nanocrystals on one hand, and by the complexity of the crystal structures on the other hand. At this point, theoretical approaches, especially the parameter-free first-principles methods, are very appropriate for finding optimal compositions and lowest-energy crystal structures. Using a semi-empirical pair-potential approach, Xie and co-workers simulated structural properties of a series of γ-$M_{23}C_6$ (M = Cr, Mn, Fe) phases [12–15]. Dos Santos performed first-principles' calculations of the electronic structure of γ-Cr_4C with a Cr fcc-based sublattice, in order to understand the electronic properties of γ-$Cr_{23}C_6$ [16]. Jiang performed a first-principles study on the structural, elastic and electronic properties of chromium carbides including γ-$Cr_{23}C_6$ [17]. Recently, Fang and co-workers investigated the stability and structure of γ-$Fe_{23}C_6$ employing the density-functional theory within the generalized gradient approximation (DFT-GGA) [18]. Sluiter reported results of first-principles calculations about the relative stability of a series of transition metals carbides [19]. However, no systematic study on the family of CFCC-TmC phases has been performed. Here the results of first-principles calculations on the stability and structures of the CFCC-TmC phases: γ-$M_{23}C_6$, η-M_6C and its related η'-$M_{12}C$, as well as π-$M_{11}C_2$ (M = Cr, Mn, Fe), are presented. The present calculations provide basis for large-scale molecular-dynamics simulations for the related alloys and steels employing semi-empirical methods, such

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as the pair-potential approximations (PPA) [12–15] and the modified embedded atom method (MEAM) [20]. on one hand. On he other hand, the information obtained here is useful for the characterization of related multi-element alloys [1,2,6,20–22], and for the development of nano-sized CFCC-TmC precipitates in steels and iron alloys [1–4,11,23,24].

2. Details of the theoretical method

The formation energy (ΔE_f) per atom of a transition metal carbide (M_nC_m) relative to the pure solids of the elements (bcc-M, M = Cr, Mn and Fe, and graphite) can be described as:

$$\Delta E_f = \{E(M_nC_m) - (nE(M) + mE(C))\}/(n + m) \quad (1)$$

At ambient conditions at the ground state (with temperature at zero Kelvin and pressure at zero bar), the enthalpy is equal to the energy, that is $\Delta H_f(M_nC_m) = \Delta E_f(M_nC_m)$, when we ignore the zero-point vibration contribution. ΔE_f is used to assess the stability of the carbide.

The VASP code using the density functional theory (DFT) within the Projector-Augmented Wave (PAW) method [25] was used for all the calculations. The (spin-polarized) generalized gradient approximation (GGA) was employed for the exchange and correlation energy terms [26], because the GGA approximation describes spin-polarized 3d transition metals such as Fe better than the local- (spin-polarized) density approximation (LDA) [27]. The cut-off energy of the wave functions was 500 eV for the 3d transition metal carbides. Reciprocal space integrations were carried out using dense *k*-meshes, e.g. $8 \times 8 \times 8$ to $12 \times 12 \times 12$ grids in the irreducible Brillouin zone (BZ) of the CFCC-TmC phases using the Monkhorst and Pack method [28].

3. Calculated results and discussion

Table 1 lists the calculated lattice parameters, compared with available experimental and former theoretical results in the literature. The calculated atomic coordinates of the CFCC-TmC phases having high-stability are included in Table 2. The calculated lattice parameters for γ-$M_{23}C_6$ are slightly smaller than the experimental values [6,10,11,18] but within 2%. Fig. 1 shows the calculated formation energies of the CFCC-TmC phases relative to the elemental solids (bcc-M, M = Cr, Mn and Fe; and graphite). Only formation energies with values smaller than 300 meV/atom are shown. Below we will discuss the formation energies and the structural and magnetic properties per CFCC-Tm phase.

3.1. The η-M_6C and related η'-$M_{12}C$ phases

The space group of η-M_6C or more generally η-$(M,M')_6C$ phases is *Fd*3*m* (nr. 227). There are three crystallographically different kinds of M atoms at 16d (M1), 32e (M2) and 48f (M3) sites, and one kind of C atoms at 16c sites [6,20], as shown in Fig. 2a. The C atoms are situated in the cavities formed by the M3 atoms. All M1 and M2 atoms are coordinated by 12 M atoms with M–M bonds ranging from 2.3 to 2.7 Å, while M3 is coordinated by 6 M atoms (M1 and M2) with bonds of 2.3–2.7 Å, by 8 M3 atoms with bonds of about 2.82 Å, and by 2 C atoms with M3–C bond lengths of 2.06 Å. The calculations also showed that the ground states of both η-Cr_6C and η-Mn_6C are non-magnetic while η-Fe_6C is ferro-magnetic with local moments at the Fe spheres of 2.2–2.5 μ_B (Table 3). The C atoms have a negative moment of about $-0.16\ \mu_B$/C. The calculations also show that η-Mn_6C is stable relative to the elemental solids with a formation energy of about -73 meV/atom, while η-Cr_6C and η-Fe_6C have formation energies of about +65 meV/atom and about +111 meV/atom, respectively.

It is also possible to build the η'-$M_{12}C$ structure from the η-M_6C structure by removing the C atoms at 16c and adding C atoms at the 8a sites (Fig. 2b). When comparing the calculated results of η'-$M_{12}C$ and η-M_6C, one can find that binary η'-$M_{12}C$ is less stable than the corresponding η-M_6C, as shown in Fig. 1. Only η'-$Mn_{12}C$ is stable with a formation energy slightly smaller than zero. The magnetism of the η'-$M_{12}C$ phases is also similar to that of η-M_6C. While η'-$Cr_{12}C$ and η'-$Mn_{12}C$ are still non-magnetic, η'-$Fe_{12}C$ is calculated to be ferromagnetic but with magnetic moments (1.9–2.4 μ_B per Fe) smaller than those in η-Fe_6C (2.2–2.5 μ_B per Fe), as shown in Table 3.

3.2. The γ-$M_{23}C_6$ phases

As shown in Fig. 1, γ-$Cr_{23}C_6$ and γ-$Mn_{23}C_6$ are calculated to have a very high stability. This is in good agreement with the experimental observations that both carbides and their alloys are commonly found in Cr–, Mn–, and Cr–Mn alloys [1–4,6,8,30]. γ-$Fe_{23}C_6$ has a formation energy of about 19.5 meV/atom, which is slightly smaller than that of the well-known cementite phase θ-Fe_3C [18,29,30].

Table 1
The calculated results (lattice parameters and magnetism) for the CFCC-TmC phases. NM: non-magnetic; FR: ferri-magnetic; FM: ferro-magnetic. PP: semiempirical pair-potentials; GGA: generalized gradient approximation; LDA: local density approximation.

Space group	Formula	Lattice parameter a (Å)		
		Present work (GGA–PPE)	Literature (calculations)	Literature (experimental)
*Fd*3*m* (227)	$Cr_{12}C$	10.5616 (NM)		
	$Mn_{12}C$	10.3701 (NM)		
	$Fe_{12}C$	10.5736 (FM)		
*Fd*3*m* (227)	Cr_6C	10.6477 (NM)		
	Mn_6C	10.4091 (NM)		
	Fe_6C	10.6503 (FM)		
*F*23 (196)	$Cr_{11}C_2$	10.7154 (NM)		~10.75[8]
	$Mn_{11}C_2$	10.8459 (FR)		~10.75[8]
	$Fe_{11}C_2$	10.7260 (FM)		
Fm$\bar{3}$*m* (225)	$Cr_{23}C_6$	10.5280 (NM)	10.903 (PP)[12,15]	10.659[6,36]
			10.53 (GGA)[17]	
			10.43 (LDA)[17]	
	$Mn_{23}C_6$	10.3966 (FR)	10.729 (PP)[15]	10.585[6]
	$Fe_{23}C_6$	10.4668 (FM)	10.627 Å (PP)[13,14]	10.639[10,11]
			10.4668 (GGA)[18]	
	$Cr_{22}C_6$	10.4817 (NM)		
	$Mn_{22}C_6$	10.3119 (FR)		
	$Fe_{22}C_6$	10.4139 (FM)		