First Principles Study of Structural Stability and Magnetic Property of Non-equilibrium Co–Mo Alloys

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Abstract First principles calculations are carried out to investigate the structural stability of several non-equilibrium intermetallic phases in the cobalt (Co)–Mo system using spin polarized projected augmented-wave potentials. It is revealed that the Co_3Mo , CoMo , and CoMo_3 alloys are energetically favored to be in D0_{19} , B11 , and A15 structures, respectively, and that the magnetic moments of Co atoms would decrease rapidly with an increasing percentage of Mo content and would most probably disappear when the content of Mo is no less than 50 at%. Generally, the calculated results in the present work match well with the available experimental observations.

KEY WORDS: First principles calculation; Transition metals; Cobalt; Magnetic property; Electronic structure

1 Introduction

Magnetic materials, i.e., Fe, cobalt (Co), and Ni-based alloys, have always been playing a significant role in the field of modern electronic engineering. In recent years, with the rapid evolution of micro-electromechanical systems and magnetic storage devices, much research has been done on the influence of the presence of nonmagnetic elements upon the magnetic properties of Co-based alloys [1–4]. From previous studies of the Co–Mo system, it is found that alloying with nonmagnetic Mo can not only modify the magnetism of Co-based alloys but also improve their hardness and corrosion resistance [5–7]. These characteristics make Co–Mo alloys one of those promising materials for microelectronic applications.

The stability of alloy phases in the Co–Mo system has thus become a fascinating scientific issue, especially since early 1980s when the solid-state reaction (SSR) and ion beam mixing (IBM) of multilayers, as well as some other far-from-equilibrium processing have successively been introduced to synthesize non-equilibrium alloy phases [8, 9]. These non-equilibrium alloy phases show great promise to adjust the magnetic property of the materials by modifying the interaction between magnetic and nonmagnetic atoms [10]. Over the intervening years, using various theoretical methods, such as thermodynamic and *ab initio* calculations, quite a few computational studies have been devoted to searching for the energetically favorable non-equilibrium phases in binary metal systems, in order to provide a basis for the conduction of experimental research [11–16]. However, yet little has been done to investigate the non-equilibrium alloy phases in Co–Mo system.

Therefore, theoretical investigation of the non-equilibrium alloy phases in the Co–Mo system was conducted in the present work, through which a plausible prediction about the relative stability and magnetic property of non-equilibrium Co–Mo alloys could be made. In order to clarify the underlying physics at a depth of electronic

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Fig. 1 The crystal structures discussed in the present work, calculations are carried out for A15, D0₃, D0₉, D0₁₉, and L1₂ structures at Co₃Mo and CoMo₃, and for B1, B2, B3, B8₁, and B11 structures at CoMo

structure, we conducted the first principles calculations to investigate the total energy and magnetic moment of several chosen alloy phases, their elastic properties and electronic density of states (DOS) were also explored to further understand this transition metal system.

2 Models and Method

In the present work, three representative alloy compositions, i.e., Co₃Mo, CoMo, and CoMo₃, were selected, and some relatively simple structures, i.e., A15, D0₃, D0₉, D0₁₉, and L1₂ at Co₃Mo and CoMo₃, and B1, B2, B3, B8₁, and B11 at CoMo (see Fig. 1), were calculated. These structures were chosen based on the following considerations: first, complicated structures usually correspond to large unit cells containing more atoms than simple ones, thereby requiring a larger critical radius for nucleation and growth of the phase. Consequently, a high temperature and a presumably long time are needed to enhance the atomic mobility in the lattice so as to rearrange the atoms in a highly ordered way. If sufficient kinetic conditions are out of reach, these complicated structures can hardly be formed. Secondly, in the past 20 years, many experimental results obtained by far-from-equilibrium processes, such as SSR and IBM, have indicated that simple structures are more favorable than complicated ones in non-equilibrium states. Researchers tend to believe that the restricted kinetic conditions involved in the process (SSR or IBM) are the main reason for this preference [17]. The following fact may support this argument. It is reported that ion

irradiation of the Ni₅₀Mo₅₀ multilayer resulted in the formation of a metastable hexagonal phase, instead of the most stable equilibrium δ phase [18]. As the δ phase has been characterized to be a very sophisticated and ordered orthorhombic structure with 56 atoms in a unit cell, it was the structural complexity that prevented it from forming upon a restricted kinetic condition. Based on the aforementioned considerations, the selection of crystal structures in the present work can be regarded as a feasible one, which can effectively reduce the required amount of computation.

A pseudopotential plane-wave method, i.e., Vienna ab initio simulation package (VASP) using the projected augmented wave (PAW) basis, was employed to conduct the calculations [19–23]. The exchange-correlation functional is a semilocal generalized gradient approximation (GGA) proposed by Perdew *et al.* [24]. The VASP-PAW-GGA method, which approaches the accuracy of all-electron methods with the efficiency of pseudo-potentials, is generally considered as a reliable electronic structure method in treating the transition metals [22]. We considered nine valence electrons for Co ($3d^7 4s^2$) and six for Mo ($4d^5 5s^1$) in the present work. An energy cutoff of 430 eV was used for the plane-wave basis, while the integration in the Brillouin zone was done on special k points determined by the Monkhorst–Pack scheme [25]. Energy convergence in terms of k points has been reached so that it has a minimal effect on the calculation results. The internal atomic coordinates and the lattice parameters were also relaxed by structural optimizations and the total energy calculations converged to less than 1 meV/atom.

3 Results and Discussion

For the possible Co_3Mo phase, we carried out the spin polarized (SP) and non-SP (NSP) calculation of the total energy of each structure. It is noted that the total energy of the respective structures obtained by SP calculation is lower than that by NSP calculation, indicating that all the calculated structures tend to be SP at 0 K. That is to say, magnetization, which results from spin polarization of the electrons or the nuclei, could stabilize the Co_3Mo alloy phases to some extent. Therefore, we used the SP calculation results to investigate the stability of the five structures mentioned above. The calculated properties of each structure are listed in Table 1. Apparently, D0_{19} structure has the lowest total energy among the five structures, indicating that it is the most energetically favored structure. As for the remaining four structures, the L1_2 structure has the second lowest total energy that is very close to that of D0_{19} , while D0_9 structure has the especially high total energy, also the highest among the selected structures, suggesting that D0_9 structure is relatively unstable and has little chance to be formed. In addition, the calculated lattice constants of D0_{19} structure ($a = 0.510$ nm, $c/a = 0.80$) are in good agreement with the experimental values ($a = 0.51245$ nm, $c/a = 0.8025$) [26]. The relative error is less than 0.5%, reflecting the accuracy of the calculation performed in the present work. Besides, it is worth noting that the total energy difference between the SP and NSP calculation results (e.g., 68 meV/atom for A15 structure) may surpass the energy difference between two structures (e.g., 60 meV/atom between D0_{19} and L1_2), thus leaving room for altering the relative stability when magnetic interactions are taken into account. Although this is not presented in the present work, the consideration of magnetism will be much advantageous in finding the most stable structure of magnetic materials.

Referring to the magnetic properties illustrated in Table 1, it is shown that the magnetic moments of Co atoms for all the structures except for A15 and D0_3 are predicted to be less than $1 \mu_{\text{B}}$ /atom, which is much lower

than that of a single-crystal Co ($1.71 \mu_{\text{B}}$) [27]. The calculated results are thus in accordance with both the experimental observation and a mean-field model proposed by Shan *et al.* [28], indicating that the magnetic moment of Co atoms would decrease rapidly with an increasing number of Mo neighbors. In Shan's work, compositional dependence of magnetism for Co–Mo system was illustrated, and the magnetic moment of Co_3Mo deduced from experimental results turned out to be $0.31 \mu_{\text{B}}$ /atom, close to the *ab initio* calculated value ($0.23 \mu_{\text{B}}$ /atom) for D0_{19} structure (also the structure in equilibrium) in the present work. Their results also showed that magnetism of Co atoms would disappear when the content of Mo is higher than 50 at%, which will be demonstrated by our first principles calculations in the following paragraphs.

Unlike the Co_3Mo phase which is equilibrated in D0_{19} structure as seen in Co–Mo phase diagram, CoMo and CoMo_3 at 0 K depicted in the phase diagram are located in a two-phase region where the phases on both sides have different crystal structures [5]. For the metastable CoMo phases, the SP calculations are carried out for five selected possible structures, i.e., B1, B2, B3, B8_1 , and B11, and presented in Table 2. It turns out that among the five structures, the most stable one is B11. Nevertheless, the difference between the total energy of B11 structure and that of the equivalent amount of elements in standard element reference states (hcp for Co and bcc for Mo) is quite large being 0.149 eV/atom compared with that of Co_3Mo in D0_{19} structure (-0.044 eV/atom), bringing on the anticipation that a considerably large amount of energy provided by far-from-equilibrium processing is indispensable for the formation of this highly energetic metastable CoMo alloy. It is noted from Table 2 that the magnetism of B11 structure, as well as the B1 and B3 structures, is infinitesimal in the acceptable error range of the computation. Consequently, these structures can roughly be regarded as nonmagnetic. Thus, we predict that the energetically stable phase among five calculated structures is the nonmagnetic B11. The loss of magnetism in $\text{Co}_{0.5}\text{Mo}_{0.5}$ alloy is confirmed by Shan's experiments mentioned above

Table 1 Calculated properties of Co_3Mo , including lattice constants (a and c), atomic volume (V), total energy per atom (E), and magnetic moments per atom of Co and Mo (M_{Co} and M_{Mo}), in the A15 , D0_3 , D0_9 , D0_{19} , and L1_2 structures arranged in the order of relative stability (from the most stable to the least stable)

Structures	a (nm)	c (nm)	V (10^{-3} nm^3)	E (eV)	M_{Co} (μ_{B})	M_{Mo} (μ_{B})
D0_{19}	0.510	0.408	11.48	−8.113 (−8.108)	0.40	−0.20
L1_2	0.359		11.52	−8.606 (−8.058)	0.28	−0.13
A15	0.458		11.99	−7.950 (−7.882)	1.03	−0.28
D0_3	0.574		11.82	−7.840 (−7.823)	1.34	−0.07
D0_9			21.61	−5.970 (−5.941)	0.58	−0.17

In the round bracket, the values of E are derived from non-spin polarized calculations. A negative value of the magnetic moment of Mo atoms means that it is in the opposite direction to that of Co atoms

Table 2 Calculated properties of CoMo, including lattice constants (a and c), atomic volume (V), total energy per atom (E), and magnetic moments per atom of Co and Mo (M_{Co} and M_{Mo}), in the B1, B2, B3, B8₁, and B11 structures arranged in the order of relative stability (from the most stable to the least stable)

Structures	a (nm)	c (nm)	V (10^{-3} nm ³)	E (eV)	M_{Co} (μ_{B})	M_{Mo} (μ_{B})
B11	0.309	0.548	13.12	−8.878	0.00	0.00
B8 ₁	0.268	0.851	13.19	−8.778	0.55	−0.05
B2	0.297		13.15	−8.728	1.49	0.42
B1	0.485		14.24	−8.244	0.02	0.00
B3	0.525		18.09	−7.653	0.00	0.00

A negative value of the magnetic moment of Mo atoms means that it is in the opposite direction to that of Co atoms

Table 3 Calculated properties of CoMo₃, including lattice constants (a and c), atomic volume (V), total energy per atom (E), in the A15, L1₂, D0₃, D0₁₉, and D0₉ structures arranged in the order of relative stability (from the most stable to the least stable)

Structures	a (nm)	c (nm)	V (10^{-3} nm ³)	E (eV)
A15	0.486		14.37	−9.920
L1 ₂	0.386		14.35	−9.781
D0 ₃	0.614		14.46	−9.741
D0 ₁₉	0.554	0.435	14.45	−9.722
D0 ₉	0.445		22.00	−7.813

[28], suggesting that magnetism would approach zero when the content of Mo surpasses that of its counterpart. On the other hand, the magnetic moment of Co atoms for B2 structure is calculated to be 1.49 μ_{B} /atom, which is an exceptionally high value compared to other selected structures.

For the possible non-equilibrium CoMo₃ phases, calculation results are presented in Table 3. As for the order of the relative stability for the five structures, it is found that A15 structure has the lowest total energy, while D0₉ structure, again, has a much higher total energy than the others. The total energy of the L1₂ structure, the second lowest among the five, is substantially higher than that of the A15 structure, indicating that A15 structure has much greater possibility to be formed by far-from-equilibrium processing than the other structures. With the increased percentage of Mo content, it is found that the magnetic moments of Co atoms of all the five calculated structures turn out to be zero within the error range of the computation. Again, our ab initio calculated results are in perfect agreement with Shan's work. One could anticipate that magnetism would vanish ever since the content of Mo is above 50 at%, which is a surprising result comparing to that of the Co–Pd, Co–Ag, and Co–Cu systems [28, 29], where Co atoms show ferromagnetism when the content of Pd, Ag, or Cu is above 90 at%. A similar phenomenon to the case of Co–Mo was found in the Co–W system [30], in

which the magnetic moment of the Co sites decreases sharply with the increase of W, indicating that both W and Mo atoms might exert a strong effect on the magnetism of Co atoms.

In order to clarify whether the Co–Mo alloys with different structures studied in the present work are dynamically stable in the bulk form, analysis for the elastic constants is performed. By calculating the total energy as a function of appropriate lattice deformations, one can get a full set of elastic constants using the following formula [31, 32]

$$E(V, \{e_i\}) = E(V_0, 0) + \frac{V_0}{2} \sum_{ij} C_{ij} e_i e_j + \dots, \quad (1)$$

where V_0 is the volume of the original crystal with corresponding energy $E(V_0, 0)$, C_{ij} s are the single-crystal elastic constants, $\{e_i, e_j, \dots\}$ presents the members of strain tensor.

For structures with cubic lattice symmetry, there are three single-crystal elastic constants, C_{11} , C_{12} , and C_{44} , and the elastic stability criteria are: $C_{11} > 0$, $C_{12} > 0$, $(C_{11} - C_{12}) > 0$, $C_{44} > 0$. For structures with tetragonal and hexagonal lattice symmetry, there are six single-crystal elastic constants, C_{11} , C_{12} , C_{13} , C_{33} , C_{44} , and C_{66} , and the requirements of elastic stability for tetragonal crystal are: $C_{11} > 0$, $C_{12} > 0$, $C_{13} > 0$, $C_{33} > 0$, $C_{44} > 0$, $C_{66} > 0$, $(C_{11} - C_{12}) > 0$, $(2C_{11} + C_{33} + 2C_{12} - 4C_{13}) > 0$ and $(C_{11} + C_{33} - 2C_{13}) > 0$, while those for hexagonal crystal are: $(C_{11} - C_{12}) > 0$, $(C_{11} + C_{12} + C_{33}) > 0$, $(C_{11} + C_{12})C_{33} > 2C_{13}^2 > 0$, and $C_{44} > 0$. The calculated C_{ij} are listed in Table 4. For Co₃Mo, only D0₁₉ and L1₂ structures satisfy the criteria of elastic stability, indicating that the A15, D0₃, and D0₉ phases that are energetically less stable would be dynamically unstable as well. Similarly, the high-energy structures for CoMo and CoMo₃, i.e., B1, B2, B3, and D0₉, respectively, also fail to meet the criteria of elastic stability, implying that the energetically unfavorable structures are most probably to be dynamically unstable, thus discouraging the synthesis of these phases in experiment. On the other hand, the energetically favored D0₁₉-

Table 4 Calculated elastic constants (C_{ij}) of the structures studied in the present work (in 10^5 MPa)

Phases	Structures	C_{11}	C_{33}	C_{44}	C_{66}	C_{12}	C_{13}
Co ₃ Mo	D0 ₁₉	4.72	5.01	1.39	1.10	1.95	1.70
	L1 ₂	3.99		1.75		2.02	
	A15	3.95		−0.90		1.62	
	D0 ₃	2.06		1.38		2.81	
	D0 ₉	1.79		−0.11		0.23	
CoMo	B11	2.97	4.09	1.19	0.85	2.88	1.87
	B8 ₁	3.18	4.08	0.25	0.69	2.68	1.69
	B2	1.36		0.57		3.20	
	B1	3.18		−0.21		1.64	
	B3	0.96		−0.98		1.58	
CoMo ₃	A15	4.73		0.85		1.63	
	L1 ₂	2.73		1.05		2.55	
	D0 ₃	2.98		0.89		2.48	
	D0 ₁₉	3.24	3.46	0.55	0.19	2.15	2.20
	D0 ₉	2.42		−0.27		0.72	

Co₃Mo, B11-CoMo, and A15-CoMo₃ phases are expected to be dynamically stable and experimentally accessible, as shown in the present work.

Next, the electronic structure will be inspected to better understand the structural stability of Co–Mo alloys. The total and partial DOSs [eV/formula unit (f.u.)] of Co₃Mo are depicted in Fig. 2. The origin of energies along the x axis is taken with respect to the Fermi energy. As a common feature for the five structures, the DOS is all dominated by Co 3d bands which exhibit some hybridization with Mo 4d states, while only a small contribution to the total DOS is made by the Co and Mo s -electrons which are not shown in the figure. The total valence bandwidth is around 8 eV for all the structures except for D0₉, the least stable one, which has a much narrower bandwidth (only 5.2 eV), and thus a DOS curve located at higher energy range than the other four. It has been widely accepted that the location of Fermi level and the value of DOS at the Fermi level bear some correlation with the structural stability [33, 34]. And we can see that the Fermi level of the most stable structure, i.e., D0₁₉, is located right in a pseudo-gap, in comparison with that of D0₃ and D0₉ structures. On the other hand, it is well known that D0₁₉ and L1₂ are very much alike in atomic configurations, while the smaller DOS at the Fermi level for D0₁₉ (2.04 states/eV/f.u.) would tend to render it energetically more favorable than L1₂ (3.12 states/eV/f.u.), which is consistent with the calculated results of the total energy described above.

From the partial DOS shown in Fig. 2, it is noticed that the DOS on Mo atoms is not identical for both spin channels. This suggests that there would be magnetic effects induced by Mo atoms. The result is in consistent

Fig. 2 Total density of states (DOS, states per eV per formula), partial DOS of the Co 3d (blue dash dot line), and Mo 4d (red short dash line) electrons of Co₃Mo in the A15, D0₃, D0₉, D0₁₉, and L1₂ structures (the Fermi level is at the energy of zero)

with the calculated magnetic moments listed in Table 1. For all the structures at Co₃Mo, the magnetic moments of Mo atoms are in opposite direction as that of Co atoms, indicating that they have ferrimagnetic properties. The same case happens for B8₁ structure at CoMo, though the magnetic moments of Mo atoms turn out to be quite small. It is also found that when the magnetic moment of Co atoms is zero, there would be no magnetism in Mo atoms as well, indicating prevailing magnetic interaction between Co and Mo atoms in the Co–Mo system.

4 Conclusions

Employing the VASP, first principles calculation results reveal that the non-equilibrium Co₃Mo, CoMo₃, and CoMo

alloys are energetically favored to be in D0₁₉, A15, and B11 structures, respectively. It is also revealed that the magnetic moments of Co atoms in Co₃Mo alloys are much lower than that of a single-crystal Co, while CoMo₃ alloys and most of CoMo alloys prefer to be nonmagnetic, suggesting that alloying Mo could probably reduce the magnetic moment of Co atoms. The magnetism of those energetically favored Co–Mo alloys would most probably disappear when the content of Mo is no less than 50 at%.

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