

First-principles prediction of partitioning of alloying elements between cementite and ferrite

Chaitanya Krishna Ande^{a,b}, Marcel H.F. Sluiter^{b,*}

^a Materials innovation institute (M2i), Mekelweg 2, 2628 CD Delft, The Netherlands

^b Dept. of Materials Science and Engineering, 3mE, Mekelweg 2, 2628 CD, Delft University of Technology, Delft, The Netherlands

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Abstract

At long tempering times in steels when both cementite (Fe_3C) and ferrite (body-centered cubic (bcc) Fe-rich solid solution) phases are present, alloying elements tend to segregate to either of the two phases. The elements V, Cr, Mn, Mo and W are found to partition to the cementite phase, while Al, Si, P, Co, Ni and Cu partition to ferrite. We show that partitioning of alloying elements and cementite (de)stabilization by alloying in mixtures of bcc Fe and cementite are intimately related through the introduction of a partitioning enthalpy. The formation enthalpy of alloying-element-substituted cementite is shown not to be a proper gauge for addressing these questions.

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1. Introduction

Cementite is the most common metastable carbide in steel. At room temperature it is ferromagnetic (FM), with a Curie temperature, T_c , of about 483 K [1,2]. Cementite has an orthorhombic crystal structure represented by Pearson symbol oP16 and space group number 62. It has 12 Fe and 4 C atoms per unit cell [2,3]. There are two inequivalent Fe positions, viz. the general and the special positions, with the Wyckoff notations 8d and 4c respectively. Carbon atoms also occupy a 4c Wyckoff site. Cementite displays many interesting properties, such as INVAR behavior [4], and is suspected to be a major component of the earth core as well [5]. Cementite can be present in various forms in steel and strongly affects its properties. The (de)stabilization of cementite plays an important role in the secondary hardening of steel [6,7], and the suppression of cementite by alloying elements is of utmost interest for transformation-induced plasticity (TRIP) steels [8,9] and for steels

based on the quenching and partitioning process [10]. In low-alloyed steels, the cementite phase usually coexists with a body-centered cubic (bcc) Fe solid solution phase, commonly referred to as ferrite. Therefore, partitioning of alloying elements and cementite (de)stabilization by alloying elements have to be regarded as a balance involving both the cementite and the ferrite phases.

Alloying element partitioning has been investigated in the past by various experimental methods. It has been consistently found that Cr [1,11–21] and Mn [1,11–16,20,22–27] partition to the cementite phase while Si [1,11,12,16,20,22–25,27–29] has a higher concentration in the bcc Fe phase. There also have been (less extensive) investigations that indicate that Al [30], Co [16] and Cu [26] partition to the bcc Fe phase while V [1,13,16,22,31], Mo [1,15,16,20,22,32] and W [16,32] preferably dissolve in the cementite phase. It is not necessary for all the alloying elements to partition either to the bcc Fe or the cementite phase: depending on the concentration of alloying elements used and the processing conditions, alloying elements like Ti, Nb and V [1,13,16,22,31] form very stable NaCl-type carbide phases, P segregates to grain boundaries [33,34], and Al might combine with oxygen and nitrogen to form

* Corresponding author. Tel.: +31 15 2784922; fax: +31 15 2786730.

E-mail addresses: C.Ande@m2i.nl (C.K. Ande), M.H.F.Sluiter@tudelft.nl (M.H.F. Sluiter).

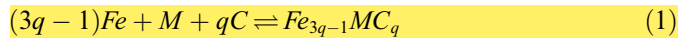
aluminum oxide and aluminum nitride respectively. S is usually bound by Mn in the form of MnS and is not present in sufficient amounts to actually partition to either of the phases. Hence, from the experimental data, partitioning of Ti, P and S in particular remain rather unclear.

Partitioning has been studied theoretically also by computing enthalpy changes upon substitution of Fe atoms by alloying elements on the Fe sublattices in cementite. The (de)stabilization of cementite by 3d and 4d transition elements was investigated by Shein et al. [35]. They report that Sc, Ti, V, Cr, Zr and Nb stabilize cementite while Ni, Cu, Pd and Ag destabilize it. Jang et al. [36,37] report that cementite is stabilized by Mn and destabilized by Si. Both Shein et al. [35] and Jang et al. [36,37] attribute the (de)stabilization of cementite to the formation enthalpy of the alloying-element-substituted cementite. Zhou et al. [38] find a positive formation enthalpy for Cr substituted cementite and they conclude that Cr substitution destabilizes cementite. Medvedeva et al. [39], however, report that Cr substitution increases the cohesive energy, which they interpret as a stabilization of cementite.

In this communication we calculate both formation enthalpies and partitioning enthalpies, as defined below, considering both FM and non-magnetic (NM) cementite with alloying element substitutions. We show that partitioning enthalpies generally describe the partitioning of alloying elements between bcc Fe and cementite in agreement with experiments, while the formation enthalpies do not. Finally, we point to some remaining disparities in the calculated partitioning behavior.

2. Methodology

The balance for the formation of alloying-element-substituted cementite from the elements,



gives the formation enthalpy as

$$H_f = H[Fe_{3q-1}MC_q] - (3q - 1)H[Fe] - H[M] - qH[C] \quad (2)$$

where M is an alloying element substituting one Fe atom in cementite ($Fe_{3q}C_q$) to give the alloying-element-substituted cementite ($Fe_{3q-1}MC_q$). $H[Fe_{3q-1}MC_q]$, etc. are the total enthalpies at 0 K. The pure elements are in their standard states, i.e. Fe is FM with a bcc crystal structure, C is in the form of graphite and M is in the appropriate crystal structure at ambient temperature and pressure (see Table 1).

Previously, Jang et al. [36,37] and Shein et al. [35] have interpreted the change in the formation enthalpies of alloying-element-substituted FM cementite with respect to FM cementite,

$$\Delta H_f^{FM} = H_f[Fe_{3q-1}MC_q^{FM}] - H_f[Fe_{3q}C_q^{FM}] \quad (3)$$

as a gauge whether M partitions to, and stabilizes, cementite. As cementite is only a weak ferromagnet with a low

Table 1

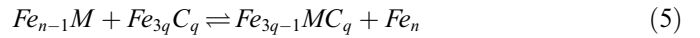
Enthalpies at 0 K of the elements in their standard states, $H[M]$.

M	Pearson symbol	$H[M]$ (eV atom ⁻¹)	M	Pearson symbol	$H[M]$ (eV atom ⁻¹)
Al	cF4	-3.697	Fe	cI2	-8.208
Si	cF8	-5.432	Co	hP2	-7.015
P	oC8	-5.369	Ni	cF4	-5.464
S	oF128	-4.110	Cu	cF4	-3.728
Ti	hP2	-7.775	Nb	cI2	-10.063
V	cI2	-8.926	Mo	cI2	-10.807
Cr	cI2	-9.470	W	cI2	-12.923
Mn	cI58	-8.982	C	hP4	-9.118

Curie temperature, it is worthwhile also considering it in the NM state (see below),

$$\Delta H_f^{NM} = H_f[Fe_{3q-1}MC_q^{NM}] - H_f[Fe_{3q}C_q^{NM}] \quad (4)$$

In a steel the alloying elements, at sufficiently low concentrations, are generally not in their elemental states, but are dissolved either in bcc Fe or in cementite. Hence, it is obviously not appropriate to take M in its standard state as a reference state. A more appropriate balance to study the alloying element partitioning and the (de)stabilization of cementite can be given as



where $Fe_{n-1}M$ and Fe_n represent the alloying element dissolved in bcc Fe and pure bcc Fe respectively. This gives the partitioning enthalpy per M atom as

$$H_p = H[Fe_n] + H[Fe_{3q-1}MC_q] - H[Fe_{n-1}M] - H[Fe_{3q}C_q] \quad (6)$$

Stabilization entails a transfer of M from the solid solution of M in bcc Fe to the cementite phase while destabilization implies that the alloying element remains in the bcc Fe solid solution. Therefore, the (de)stabilization of cementite has to be regarded as a competition between cementite and bcc Fe, and the latter contribution is missing from the cementite formation enthalpies defined above. It follows that a (positive) negative H_p , rather than a (positive) negative H_f , implies that the alloying element (de)stabilizes and partitions to (bcc Fe) cementite.

First-principles density functional calculations yield enthalpies at 0 K. In the case of cementite and bcc Fe, these enthalpies are for the FM state. At the typical tempering temperatures used in experiments (600–950 K), cementite is no longer in the FM state, while bcc Fe is still well below its Curie temperature (bcc Fe, $T_c = 1043$ K). It might thus be more appropriate to use the enthalpy of the disordered magnetic state for cementite. Here, we consider that the enthalpy of magnetically disordered cementite shifts slightly in the direction of that of the NM state – though without actually reaching the NM enthalpy because local magnetic moments on Fe atoms typically persist to well above the Curie temperature. Khmelevskiy et al. [40] have argued that the disordered magnetic state and the NM state in cementite are almost degenerate in energy, although they

base their argument on GGA energies derived from LDA charge densities. Nevertheless, the FM and the NM enthalpies may be regarded as the upper and lower limits for the cementite enthalpy in the vicinity of, and above, T_c .

At finite temperatures the partitioning free energy, rather than the partitioning enthalpy, should be used. One approach to obtain the free energy of partitioning is to use the experimental heat capacity data of cementite with alloying elements. Unfortunately, there is little experimental data on the heat capacity of cementite. Reliable heat capacity data on alloyed cementite is almost non-existent. The second approach is to compute the free energy directly from the first-principles calculations. Recently, progress has been made in this area for bcc Fe [41] and even for pure cementite [42], though it is presently still out of reach for alloying-element-substituted cementite. However, considering that we expect entropy changes per M atom for the balance in Eq. (1) to be a few k_B at most, as is typical of vibrational, configurational and magnetic transitions, and given that the contributions on either side of the balance largely cancel each other out, it follows that below 1000 K the entropy contribution (TS) is about $100 \text{ meV atom}^{-1}$ at most. We will show that for most of the alloying elements the partitioning enthalpy is larger than $100 \text{ meV atom}^{-1}$ so that definite conclusions can be drawn without specifically considering the entropic contributions.

2.1. Computational details

We used the spin-polarized generalized gradient approximation to density functional theory (DFT) [43,44] and a plane wave basis with a kinetic energy cut-off of 400 eV. The Kohn–Sham equations were solved using the Vienna Ab Initio Simulation package (version 4.6.34) [45–47]. The valence electron and core interactions were described using the projector augmented wave method (PAW) [48]. The first-order Methfessel–Paxton method was used with a smearing width of 0.1 eV. The PW91 exchange–correlation functional [49] with the Vosko–Wilk–Nusair interpolation [50] for the correlation part was used. The relaxations were assumed to have converged when the energy in two consecutive ionic relaxation steps differed by less than $10 \text{ } \mu\text{eV}$. For accurate bulk energies, a final calculation was done without any relaxation using the linear tetrahedron method with Blöchl corrections for smearing. Integrations in reciprocal-space employed Monkhorst–Pack sampling [51] such that the product of the number of k -points in the first Brillouin zone and the number of atoms in the supercell equalled about 10,000. Both the k -point density and energy cut-off were verified to give total energy convergence of 1 meV or better.

Pure elements were modeled using the unit cells (or primitive cells when possible) of their respective crystal structures (Table 1). Co and Ni were considered FM and Cr was considered anti-ferromagnetic (AFM). It is well-known that current DFT exchange–correlation functionals

do not model graphite accurately. To overcome this shortcoming, the total enthalpy of diamond was computed and a correction of -17 meV was added to account for the diamond to graphite transformation [52].

bcc Fe was modeled with a 54 atom supercell, Fe_{54} , consisting of $3 \times 3 \times 3$ bcc Fe unit cells with a total enthalpy of -443.295 eV at 0 K. The dilute impurity solid solution was modeled by substituting an Fe atom with the alloying element, M , giving a composition $Fe_{53}M$ (see Table 2). Reciprocal space integrations employed a $6 \times 6 \times 6$ k -point grid.

Cementite was modeled as a unit cell with 16 atoms, $Fe_{12}C_4$, and an $8 \times 6 \times 10$ k -point grid was used for integrations. Alloying-element-substituted cementite was modeled by replacing one of the Fe atoms in the unit cell with the alloying element, $Fe_{11}MC_4$. We considered the alloying element substituting the Fe atom at both the general and the special positions. Both the FM and AFM configurations of the Fe atoms on the two sites were considered.

The magnetic moments on the atoms were calculated by integrating the spin densities inside the PAW spheres of the respective atoms. Finally, enthalpies for NM cementite were calculated by switching off spin-polarization.

3. Results and discussion

As dilute substitutional impurities in bcc Fe, Al, Si, P and S have negligible moments (see Table 2). Both 3rd and 4th row transition elements having fewer than five d-electrons (Ti, V, Cr, Nb, Mo, W) align AFM with increasing magnitude of moments to the surrounding Fe atoms. Alloying elements with more than six d-electrons (Co, Ni) align FM with decreasing magnitude of moments. With the exception of Mn (five d-electrons), the magnetic moments on all the impurity atoms in bcc Fe agree well with those reported by Drittler et al. [53]. The magnetic state of Mn in bcc Fe is sensitive to lattice parameter. We find that Mn aligns AFM when the bcc lattice parameter exceeds 0.282 nm.

The magnetic alignment of all the alloying elements in cementite (except for Mn) is comparable to that of bcc Fe. Al, Si, P and S have negligible magnetic moments (Table 3). Early transition elements, like Ti, V, Cr, Nb, Mo and W, align AFM to the surrounding Fe atoms, while

Table 2

Enthalpies at 0 K of bcc Fe supercells with respect to the Fe_{54} supercell, $\Delta H[Fe_{53}M] = H[Fe_{53}M] - H[Fe_{54}]$ and the magnetic moment on M , μ_M .

M	$\Delta H[Fe_{53}M]$ (eV)	μ_M (μ_B)	M	$\Delta H[Fe_{53}M]$ (eV)	μ_M (μ_B)
Al	3.751	−0.07	Fe	0.000	2.21
Si	1.661	−0.08	Co	1.069	1.69
P	1.842	−0.05	Ni	2.844	0.89
S	4.314	0.02	Cu	5.217	0.11
Ti	−0.394	−0.76	Nb	−1.992	−0.73
V	−1.453	−1.21	Mo	−2.575	−0.76
Cr	−1.412	−1.69	W	−4.796	−0.76
Mn	−0.522	−1.82			

Table 3

Formation and partitioning enthalpies, H_f and H_p , respectively, at 0 K. Magnetic moments, μ_M , on the alloying elements in cementite are also listed.

M	H_f (eV atom ⁻¹)				H_p (eV atom ⁻¹)				μ_M (μ_B)	
	FM		NM		FM		NM		4c	8d
	4c	8d	4c	8d	4c	8d	4c	8d		
Al	0.09	0.02	1.01	1.02	0.59	0.52	0.22	0.23	−0.04	−0.04
Si	0.80	0.55	1.72	1.48	1.65	1.40	1.29	1.05	−0.04	−0.06
P	1.86	0.65	2.90	1.99	2.59	1.39	2.35	1.44	0.01	−0.07
S	3.03	1.26	4.32	2.59	2.56	0.79	2.56	0.83	0.00	−0.03
Ti	−0.77	−0.78	0.14	0.15	−0.21	−0.22	−0.57	−0.57	−0.39	−0.40
V	−0.37	−0.46	0.57	0.43	0.10	0.01	−0.24	−0.38	−0.54	−0.57
Cr	0.26	0.16	1.22	1.04	0.14	0.04	−0.19	−0.36	−0.83	−0.84
Mn	0.34	0.31	1.36	1.25	−0.18	−0.21	−0.44	−0.54	1.87	1.30
Fe	0.26	0.26	1.55	1.55	0.00	0.00	−0.00	−0.00	1.92	1.83
Co	0.35	0.30	1.60	1.68	0.21	0.16	0.18	0.26	1.08	1.00
Ni	0.48	0.40	1.66	1.80	0.12	0.04	0.01	0.16	0.30	0.38
Cu	1.24	1.14	2.34	2.52	0.24	0.14	0.06	0.24	0.02	0.07
Nb	0.16	0.11	1.21	1.15	0.04	−0.01	−0.20	−0.26	−0.36	−0.38
Mo	0.50	0.44	1.56	1.44	0.22	0.16	−0.01	−0.13	−0.30	−0.34
W	0.54	0.46	1.57	1.42	0.36	0.28	0.10	−0.04	−0.31	−0.33

the late transition elements Co and Ni align FM. While Mn in bcc Fe aligns AFM, it aligns FM with the surrounding Fe atoms in cementite. The magnitude of the magnetic moments on the alloying elements is larger when substituted at the special positions than when substituted at the general position. The higher number of C atoms surrounding the alloying elements in the general position (three in the general position vs. two in special position) quench the magnetic moments of the alloying elements.

The formation enthalpy of FM cementite ($H_f[Fe_{3q}C_q^{FM}]$) is in good agreement with previous first-principles calculations. While we report a formation enthalpy of 16 meV atom⁻¹ (Table 3), Fang et al. [54] and Hallstedt et al. [42], both using similar methods as in the present communication, reported values of 20.6 and 20.7 meV atom⁻¹, respectively, at 0 K. This implies that formation of cementite is unstable with respect to the pure elements. Jang et al. [36,37], using the full potential linearized augmented plane wave (FLAPW) method and taking the total enthalpy of graphite as obtained from FLAPW as C reference, reported a formation enthalpy of 56 meV atom⁻¹. However, as the interplanar interaction in graphite is poorly described in current first-principles methods, we prefer, like Fang et al. [54] and Hallstedt et al. [42], to use the first-principles computed enthalpy of diamond and make a correction for graphite. Experimentally, Meschel and Kleppa [55] obtained a formation enthalpy of 48.7 ± 11.4 meV atom⁻¹ at 298.15 K.

Although the $H_f[Fe_{3q}C_q^{FM}]$ determined by us is lower than the experimental value of Meschel and Kleppa [55], the difference between the formation enthalpy of the Si-substituted FM cementite with respect to FM cementite (Table 3, Fig. 1) agrees well with the results of Jang et al. [36,37]. For Si substituted at the special and general sites, we obtained values of 34 and 18 meV atom⁻¹ respectively, while Jang et al. [36] obtained 34 and 24 meV atom⁻¹ respectively. The enthalpies of the reference states, $H[M]$,

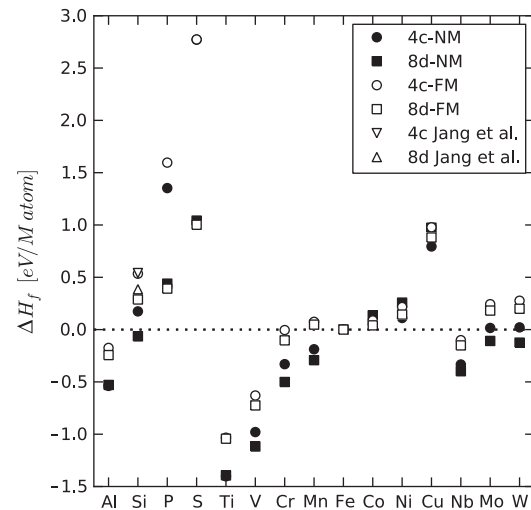


Fig. 1. Formation enthalpy change of alloying-element-substituted cementite, ΔH_f .

used in calculating the formation enthalpy, H_f , along with the Pearson symbols of their crystal structures are listed in Table 1.

The formation enthalpy change, ΔH_f^{FM} , of FM cementite (Fig. 1) is positive for Si, P, S, Mn, Co, Ni, Cu, Mo and W and negative for Al, Ti, V, Cr and Nb. Previously, Jang et al. [36,37] and Shein et al. [35] interpreted this as an indication that Si, P, S, Mn, Co, Ni, Cu, Mo and W stabilize and partition to bcc Fe while Al, Ti, V, Cr and Nb stabilize and partition to cementite. This is in disagreement with experiments for Al [30], Mo [1,15,16,20,22,32] and W [16,32]. For Mn the enthalpy changes are so small as to make interpretation ambiguous. While Jang et al. [37] find a slightly negative ΔH_f^{FM} for Mn, we find a slightly positive value. Also, Si is used as an essential alloying element in TRIP steels for its ability to strongly suppress the formation of cementite [56]. Hence, it is surprising that the

formation enthalpy of Si-, Mo- and W-substituted FM cementite are comparable. The disagreements with experiments in the cases of Al, Mo and W and the comparable formation enthalpy of Si-substituted cementite with that of Mo- and W-substituted cementite clearly show the shortcomings of using formation enthalpies (H_f^{FM}) to determine alloying element partitioning between bcc Fe and cementite.

To evaluate how stabilization and partitioning might be affected by magnetic disordering in cementite, we consider the extreme case of NM cementite. The formation enthalpy change, ΔH_f^{NM} (Fig. 1) gives increased cementite stabilization for all elements. As mentioned above, particularly for Al and Si, a movement towards stronger cementite stabilization strongly disagrees with experimental evidence as both Al and Si are used to suppress the formation of cementite in TRIP steels [56].

All the alloying elements prefer the general position over the special position in agreement with previous results [35,36]. The preference for the general position might be slightly weakened by magnetic disordering because in NM cementite Al, Ti, Co, Ni and Cu prefer to occupy the special position. However, as energy differences between the general and special positions remain small even in the extreme case of completely vanishing magnetic moments, we expect the effect to be minor.

Table 3 and Fig. 1 show that results derived from formation enthalpies do not indicate partitioning of alloying elements as observed experimentally. On the other hand, as evident from Table 3 and Fig. 2, the partitioning enthalpy H_p (Eq. (6)) calculated from total enthalpies of FM cementite correctly indicate that Si, Al, P, S, Co, Ni and Cu partition to bcc Fe and Ti, Mn and Nb partition to cementite—although V, Cr, Mo and W are probably incorrectly indicated to partition weakly to bcc Fe. Magnetic disordering of cementite, as considered through the extreme case of the NM state, is seen to favor stabilization and partitioning toward cementite. It moves the problematic elements V, Cr, Mo and W in the correct direction

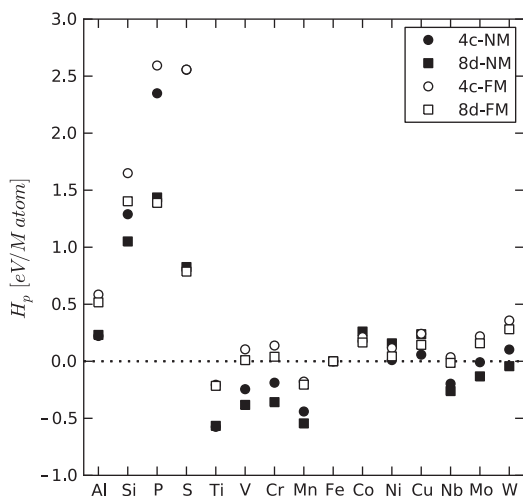


Fig. 2. Partitioning enthalpies, H_p . For the element S the 4c-FM symbol covers and obscures the 4c-NM symbol.

towards being cementite stabilizers, although W would remain on the bcc Fe side. In contrast to the formation enthalpy evaluation, Al and Si remain strongly on the bcc Fe side, as they should. A factor that can influence the experimental findings is whether cementite exists in the presence of austenite. Strong ferrite formers such as V, Mo, and W would segregate more strongly to cementite from austenite than from ferrite.

Consideration of entropy effects, as mentioned earlier, for most elements cannot affect our conclusions. Only for Ni, Cu and W is the partitioning enthalpy less than $100 \text{ meV atom}^{-1}$, so that entropy effects might affect our conclusions at finite temperature. However, even for these elements our results are in agreement with experiments.

Although partitioning of the alloying elements between the bcc Fe and cementite phases appears to be described correctly, it fails quantitatively. Experimentally, Cr has a much higher partitioning coefficient towards cementite than Mn [16]. In contrast, we find that Mn partitions stronger. It is possible that the experimental findings here, too, are affected by the much stronger austenite forming tendencies of Mn than of Cr. Second, in steel, where other phases can be present, alloying elements might partition to bcc Fe, cementite or any of the other phases and not necessarily just between bcc Fe and cementite.

4. Conclusions

Experimental findings on the partitioning of alloying elements between bcc Fe and cementite were compared with enthalpies of FM and NM alloying-element-substituted cementite. Formation enthalpies were shown to not correctly describe the (de)stabilization of cementite by, or the partitioning of, alloying elements. On the other hand, the partitioning enthalpy which describes the competition between the cementite and the bcc Fe phases gave results that generally agreed with experimental observations, particularly when the trends resulting from magnetic disordering in cementite were considered.

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